

**ELECTRON TRANSFER REACTIONS. REACTION OF NITRONES,
DIBENZOBARRELENES, EPOXYKETONES AND
BENZOYLAZIRIDINES WITH POTASSIUM**

**A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of**

DOCTOR OF PHILOSOPHY

by

K. ASHOK

to the

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

JANUARY, 1987

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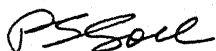
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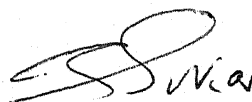
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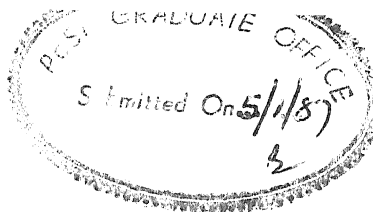
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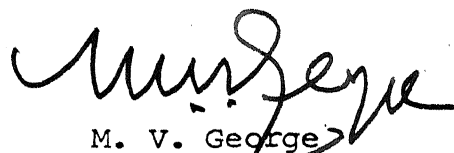
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M. V. George
Thesis Supervisor

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor M. V. George.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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K. Ashok

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K. ASHOK

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PREFACE

The thesis entitled: "Electron Transfer Reactions. Reaction of Nitrones, Dibenzobarrelenes, Epoxyketones and Benzoylaziridines with Potassium" consists of three chapters.

Chapter I deals with our studies on the potassium-induced transformations of a few nitrones and related substrates. Some of the compounds that we have examined include α ,N-diphenylnitrone (1a), α -o-hydroxyphenyl-N-phenylnitrone (1b), N-phenyl- α -p-tolyl-nitrone (1c), α -phenyl-N-p-tolyl-nitrone (1d), triphenylnitrone (26a), α -diphenylene-N-phenylnitrone (26b), N-benzyl- α -phenyl-nitrone (34), and 1,1,3-triphenylisindole N-oxide (49).

Treatment of nitrones (1a-d, 26a,b, 34, 49) with potassium in tetrahydrofuran (THF) gave a variety of products, arising through radical anion and dianion intermediates. Thus, the aldehydonitrones 1a-d gave the corresponding aldehydes 10a-c (30-42%), carboxylic acids 25a-c (44-49%), azo compounds 19a,d (69-88%) and trace amounts of stilbenes 13a-c, (4-8%), whereas the ketonitrones 26a,b gave the corresponding Schiff bases 31a,b (81%). The nitrone 34 gave a mixture of products consisting of benzoic acid (25a, 18%) dibenzyl (48, 18%), the dimeric nitrone 38 (21%), and tetraphenylpyrazine (46, 17%), along with the recovery of a small amount (8%) of the starting material (34). The reaction of the N-oxide 49, with potassium in THF, however, did not lead to any isolable product; most of the starting material (49, 69%) could be recovered unchanged.

Our studies on the reactions of several substituted dibenzobarrelenes containing 1,2-dibenzoylalkene functionalities, with potassium form the subject matter of Chapter II. The compounds that we have examined include 11,12-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (1a), 11,12-dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-ethenoanthracene (1b), 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (1c), 11,12-dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethenoanthracene (1d), 11,12-dibenzoyl-9,10-dihydro-9-phenyl-9,10-ethenoanthracene (1e) and 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (1f). In general, the reaction of dibenzobarrelenes (1a,b,d-f) with potassium gave the corresponding anthracenes (6a,b,d-f, 14-21%), dihydrodibenzobarrelenes (10a,b,d-f, 28-51%) and benzoic acid (8, 23-31%). The reaction of the dibenzobarrelenes 1a,f with potassium, on the other hand, gave the monodebenzoylated products 18a,f (14-30%), besides 6a,f, 10a,f and 8, whereas the reaction of the hydroxydibenzobarrelene 1c with potassium gave a mixture of anthracene (24, 7%), anthraquinone (25, 7%), 10-(cis-1,2-dibenzoyl-ethenyl)-9-anthrone (23, 21%), 10-(cis-1,2-dibenzoyl-ethenyl)-9-anthrol (26, 31%) and 8 (14%). The reaction of the methoxy substituted dibenzobarrelene (1d) gave a mixture of anthraquinone (25, 17%) and 2-(9-anthracenyl)-1,4-diphenyl-1-hydroxy-but-1-ene-3,4-dione (31, 17%), besides 6d, 10d and 8.

Chapter III of the thesis deals with our studies on the reaction of potassium with several oxygen and nitrogen heterocycle

containing benzoyl or dibenzoylalkene functionalities. The substrates that we have studied include trans-1,3-diphenyl-2,3-epoxypropan-1-one (1a), trans-2,3-epoxy-1-phenyl-3-p-tolylpropan-1-one (1b), 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (34a), 2,3-dibenzoyl-1,4-dihydro-1,4-diphenyl-1,4-epoxynaphthalene (34b), trans-2-benzoyl-1-cyclohexyl-3-phenylaziridine (46a), cis-2-benzoyl-1-cyclohexyl-3-phenylaziridine (46b), cis-2-benzoyl-1-cyclohexyl-3-p-tolylaziridine (46c), cis-1-cyclohexyl-2-phenyl-3-p-tolylaziridine (46d) and 1-cyclohexyl-6-(cyclohexylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-b]azirine (61). The reaction of chalcone epoxides (1a,b), for example, gave a mixture of products, such as acetophenone (13, 3-5%), the corresponding chalcones 4a,b (3-4%), dihydrochalcones 20a,b (4-5%), cyclopentene isomers 21a,b (4-11%) and 22a,b (3-11%), hydroxyacids 15a,b (26-29%) and benzoic acid (12a, 31-33%). The reaction of 34a with potassium, on the other hand, gave a mixture of o-dibenzoylbenzene (38a, 70%) and benzoic acid (12a, 15%), along with a 5% recovery of the unchanged starting material (34a). The reaction of 34b, however, gave a mixture of 1,3-diphenylisobenzofuran (40b, 41%), 2-benzoyl-1,4-diphenylnaphthalene (45b, 13%), 2,3-dibenzoyl-1,4-diphenylnaphthalene (38b, 21%), o-dibenzoylbenzene (38a, 13%) and 12a (41%).

The reaction of benzoylaziridines (46a-d) with potassium in THF gave a mixture of products consisting of stilbenes (57a,c,

29-36%), hydroxyamides (51a,c,d, 33-42%) and carboxylic acids (12a,b, 37-39%). The reaction of 1-cyclohexyl-6-(cyclohexylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-b]azirine (61), however, gave a mixture of 1-phenyl-4-cyclohexylaminoisoquinoline (64, 64%) and 2-cyclohexyl-3-hydroxy-3-phenylphthalimidine (68, 13%).

Reasonable mechanisms have been suggested to account for the formation of the different products in these reactions. To examine the involvement of oxygen in the formation of the various products, reactions of representative substrates with potassium in oxygen-saturated THF and potassium superoxide were carried out. Thus, treatment of the nitrone 1a with potassium in oxygen-saturated THF, for example, gave a mixture of trans-stilbene (13a, 8%), benzaldehyde (10a, 38%), benzoic acid (25a, 47%) and nitrobenzene (22a, 72%). Similar results were obtained, on treatment of 1a with potassium superoxide in benzene containing 18-crown-6. Similarly, the reaction of the chalcone epoxide 1a with potassium in oxygen-saturated THF gave a mixture of the chalcone 4a (3%), dihydrochalcone 20a (10%), 1,2,4-triphenylbutan-1,4-dione (32, 19%), 2-hydroxy-2,4,5-triphenyl-3(2H)-furanone (31, 8%), 2,3-dihydroxy-2,3-diphenylpropanoic acid (33, 4%) and benzoic acid (12a, 25%).

Cyclic voltammetric studies have been carried out, employing most of the substrates, to measure the reduction potentials

for both one electron and two electron processes, leading to the corresponding anion and dianion intermediates. The radical anions of all these substrates were also generated through pulse radiolysis in methanol and their absorption spectra were recorded.

Note: The numbers of the various compounds given in parentheses correspond to those given under the respective chapters.

CHAPTER I

ELECTRON TRANSFER REACTIONS. REACTION OF NITRONES WITH POTASSIUM

I.1 ABSTRACT

Potassium-induced transformations of a few nitrones and related substrates have been investigated. Treatment of nitrones (1a-d, 26a,b, 34, 49) with potassium in tetrahydrofuran (THF) gives rise to radical anion (2a-d, 27a,b, 35, 50) and dianion intermediates (3a-d, 28a,b, 36) through electron transfer reactions. These intermediates undergo further transformations to give a variety of products. Thus, the aldehydonitrones 1a-d give the corresponding aldehydes 10a-c, carboxylic acids 25a-c, and azo compounds 19a,d, whereas the ketonitrones 26a,b give the deoxygenation products 31a,b. The nitrone 34 gave a mixture of products consisting of benzoic acid (25a), dibenzyl (48), the dimeric nitrone 38 and tetraphenylpyrazine (46), whereas, the N-oxide 49 did not give any isolable product on treatment with potassium. To examine the involvement of any oxygen in the formation of the different products, reactions of representative nitrones with potassium in oxygen atmosphere and potassium superoxide were studied. Cyclic voltammetric studies have been employed to measure the reduction potentials for both one electron and two electron processes, leading to the radical anions and dianions,

respectively. These intermediates have been characterized through their electronic spectra and they were quenched by oxygen. Pulse radiolysis of the nitrones 1a-d, 26a,b, 34 and 49 also gave the corresponding radical anions 2a-d, 27a,b, 35 and 50, characterized by their spectra. Reasonable mechanisms involving radical anion and dianion intermediates and their subsequent transformations have been suggested to account for the formation of the different products in these reactions.

I.2 INTRODUCTION

Alkali metals are known to react with unsaturated organic substrates, giving rise to a variety of products. Several papers and review articles have appeared in the literature, which highlight the salient features of these studies.¹ In general, alkali metals add to unsaturated systems to give radical anion and dianion intermediates, which can undergo a variety of reactions, which include disproportionation, fragmentation, dimerization, oxidation and rearrangements. It may also be pointed out here that the radical anions and other reactive intermediates formed in these reactions are very susceptible to air-oxidation, which result in a variety of oxidative products.

Of the different organic substrates, nitrones have been of particular interest in view of the deoxygenation reactions, which are reported to occur in the presence of metals and other reagents.²⁻⁵ Only very few examples of the reaction of alkali

metals with nitrones have been reported so far.⁶⁻⁸ The reaction of α ,N-diphenylnitrone (1a) with sodium in ethanol, for example, has been reported to give N-benzylamine the reduction product.⁶ The object of the present investigation has been to examine the potassium-induced transformations of a few representative nitrones, with a view to studying the nature of products formed in these reactions and also to understand the mechanism of these transformations.

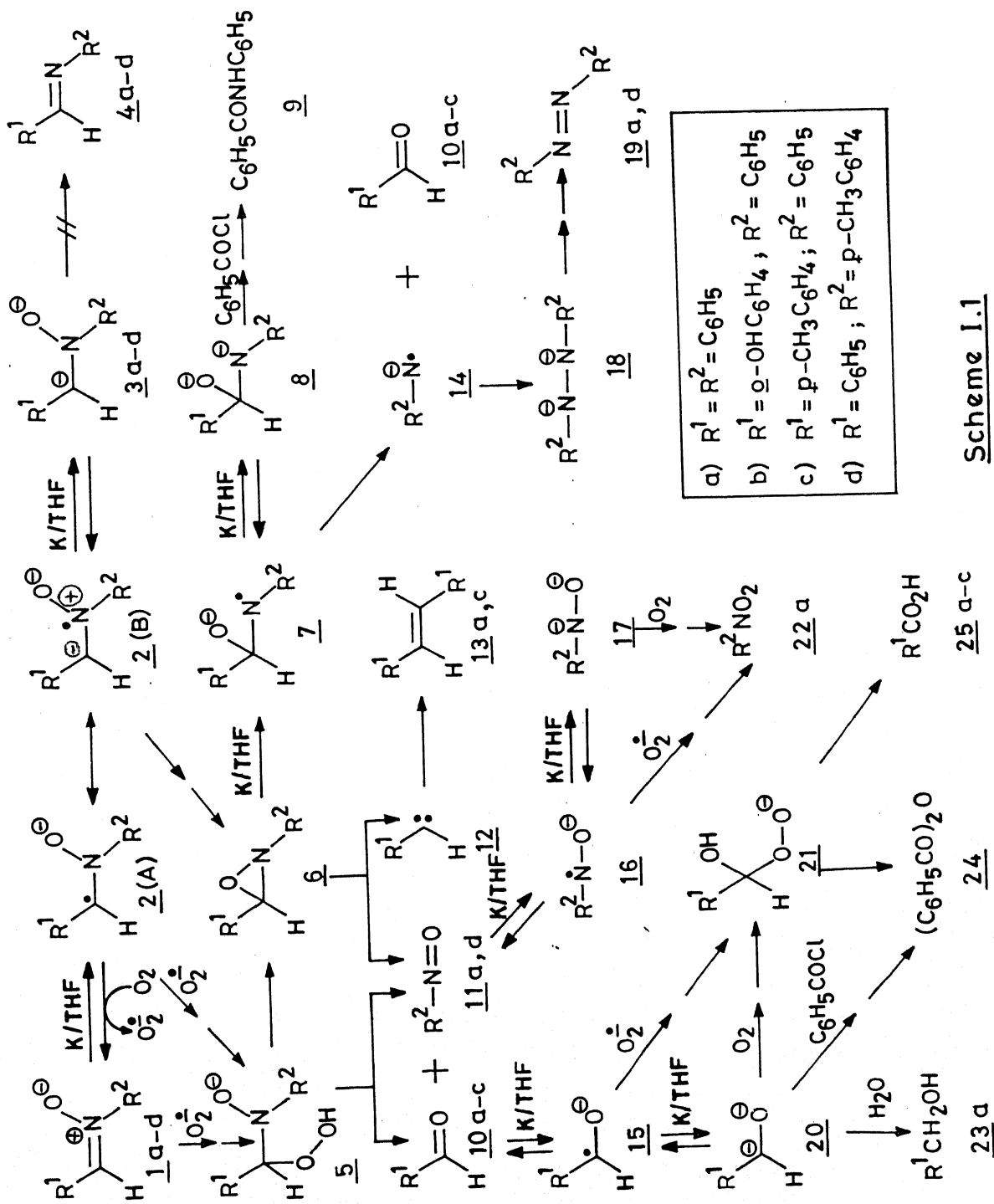
I.3 RESULTS AND DISCUSSION

In the present studies, we have examined the reactions of α ,N-diphenylnitrone (1a), α -o-hydroxyphenyl-N-phenylnitrone (1b), N-phenyl- α -p-tolylnitrone (1c), α -phenyl-N-p-tolylnitrone (1d), triphenylnitrone (26a), α -diphenylene-N-phenylnitrone (26b), N-benzyl- α -phenylnitrone (34) and 1,1,3-triphenylisoindole N-oxide (49) with potassium in THF.

The reaction of 1a with potassium in THF, for example, gave a mixture of trans-stilbene (13a, 8%), trans-azobenzene (19a, 82%), benzaldehyde (10a, 42%) and benzoic acid (25a, 47%). The reaction of 1b under analogous conditions gave a mixture of 19a (58%), salicylaldehyde (10b, 25%) and salicylic acid (25b, 30%), along with a 20% recovery of the starting material (1b). When the reaction of 1b, however, was carried out in the presence of excess of potassium (four equivalents), better yields of 19a (69%), 10b (37%) and 25b (45%) were obtained. Similarly, the reaction of 1c with potassium in THF gave a mixture of trans-1,2-di-p-tolyethylene

(13c, 6%), trans-azobenzene (19a, 80%), p-tolualdehyde (10c, 40%) and p-toluic acid (25c, 44%), whereas, 1d under similar conditions gave a mixture of trans-stilbene (13a, 4%), trans-p-azotoluene (19d, 88%), benzaldehyde (10a, 40%) and benzoic acid (25a, 49%). In contrast to the reactions of 1a-d, the reaction of triphenyl-nitrone (26a) with potassium in THF gave benzophenone anil (31a, 81%). Similarly, the reaction of 26b under analogous conditions gave a 81% yield of 9-fluorenylideneaniline (31b). When the reaction of 26b, however, was carried out in the presence of excess of potassium (4 equivalents), a mixture of 31b (71%) and 9-anilino-fluorene (33b, 8%) was obtained. On the other hand, the reaction of N-benzyl- α -phenylnitrone (34) with potassium in THF gave a mixture of benzoic acid (25a, 18%), N-(2-benzylhydroxylamino-1,2-diphenylethano)- α -phenylnitrone (38, 21%), dibenzyl (48, 18%) and 2,3,5,6-tetraphenylpyrazine (46, 17%), along with a 8% recovery of the unchanged starting material (34). The reaction of 1,1,3-triphenylisoindole N-oxide (49) with potassium in THF, however, did not lead to any isolable product; most of the starting material (49) could be recovered unchanged (69%).

The formation of the different products in the reaction of aldehydonitrones 1a-d with potassium can be understood in terms of the reaction pathway shown in Scheme I.1. It is assumed that the initial step in the reaction of 1(a-d) with potassium is an electron transfer reaction, leading to the radical anion intermediate 2(a-d) which, in turn, can accept a second electron to



Scheme I.1

give the dianion intermediate 3(a-d), depending on the ease with which 2 can be converted to 3. These dianion intermediates 3a-d could lead to deoxygenated Schiff bases 4a-d or products derived from them. In order to examine the involvement of such Schiff bases 4a-d or their further transformation products in these reactions, we have examined the reaction of N-benzylideneaniline (4a) with potassium in THF. Treatment of 4a with excess (four equivalents) of potassium in THF, under analogous conditions, gave a mixture of benzoic acid (25a, 28%) and d,l-N,N',1,2-tetraphenylethylenediamine (54, 55%). It might be mentioned in this connection that several alkali metal reactions of anils are reported in the literature.⁹ The fact that we have not been able to isolate the ethylenediamines (54) in the reaction of 1a-d would indirectly rule out the involvement of the corresponding Schiff bases (4a-d) in these reactions.

A second possible mode of reaction of 2(a-d), although less likely under our reaction conditions is its reaction with adventitious oxygen to give back the starting nitron (1a-d) and potassium superoxide. It may be mentioned in this connection that several examples of superoxide formation by electron transfer to oxygen from radical anions and also by electrochemical method are reported in the literature.¹⁰ Subsequent reaction of superoxide with 1(a-d) or 2(a-d) will lead to the hydroperoxy intermediate 5, which can fragment to the aldehyde 10(a-c) and the nitroso compound 11(a,d). Further reaction of the aldehyde 10(a-c) with potassium will give the radical anion 15 and the

dianion 20, which can ultimately lead to the corresponding carboxylic acid 25(a-c). The nitroso compound 11(a,d) in the presence of excess of potassium will lead to the azo compound 19(a,d), or in the presence of excess of oxygen give the corresponding nitro compound 22. It may be pointed out, in this connection, that nitrosobenzene, formed as an intermediate in the reaction of nitrobenzene with lithium in THF, is converted to azobenzene in the presence of excess of lithium.¹¹

A more likely pathway for the reaction of the radical anion 2(a-d) is to give rise to the oxaziridine 6, which can fragment to give the nitroso compound 11(a,d) and the carbene 12. The formation of small amounts of trans-stilbene (13a) from 1a and trans-1,2-di-*p*-tolylethylene (13c) from 1c can be explained in terms of the dimerization of 12. The oxaziridine 6 can also react further with potassium to give the radical anion 7 and the dianion 8 and ultimately products derived from them. Fragmentation of 7 can lead to the intermediate 14 and the aldehyde 10(a-c). Further transformations of 14 will ultimately give rise to the azo compound 19(a,d).

To examine whether the involvement of oxygen in the reaction of 2(a-d), as implicated earlier (Scheme I.1) can be justified or not, we have carried out, in a separate experiment, the reaction of 1a with potassium in THF, which has been previously saturated with oxygen. The reaction of 1a, under these conditions gave a mixture of trans-stilbene (13a, 8%), benzaldehyde (10a, 38%),

benzoic acid (25a, 47%) and nitrobenzene (22a, 72%). The fact that there is no appreciable difference in the yields of benzaldehyde (10a) and benzoic acid (25a), when the reaction of 1a with potassium is carried out in the absence of and in the presence of oxygen, would suggest that the pathway involving the hydroperoxy intermediate 5 in Scheme I.1 is not justified. The more likely pathway, perhaps, would be through the oxaziridine 6, as stated earlier. The high yield of nitrobenzene (22a) in the reaction of 1a with potassium in the presence of oxygen would suggest that it is formed from nitrosobenzene (11a) or other precursors such as 7, 8, and 14 through their reaction with oxygen.

To examine the type of products encountered in the reaction of the nitrones 1a-d with potassium superoxide,¹² we have carried out the reaction of 1a. Thus, treatment of 1a with potassium superoxide in benzene containing 18-crown-6 at room temperature gave a mixture of benzoic acid (25a, 82%) and nitrobenzene (22a, 89%). Also, in a separate experiment, we have shown that nitrosobenzene (11a), itself undergoes oxidation to nitrobenzene (22a, 61%), on treatment with potassium superoxide in benzene, justifying our assumption that 11a, formed through the fragmentation of hydroperoxy anion intermediate 5 is being converted to 22a.

In Scheme I.1, we have indicated the involvement of several radical anion and dianion intermediates in the transformation of the nitrones 1a-d to the observed products, on treatment with

potassium in THF. In an attempt to trap some of these intermediates, we have treated the reaction mixture from 1a (and potassium in THF), before workup, in separate experiments, with moist THF and benzoyl chloride, respectively. Treatment of the reaction mixture from 1a with moist THF, before workup gave a mixture of trans-stilbene (13a, 7%), azobenzene (19a, 78%), benzaldehyde (10a, 32%), benzoic acid (25a, 25%) and benzyl alcohol (23a, 25%). The formation of benzyl alcohol (23a) under these conditions could suggest the involvement of the dianion intermediate 20 in the transformation of benzaldehyde (10a) to benzoic acid (25a). Further, it is to be inferred that the dianion 20 is partially converted to the hydroperoxy anion intermediate 21, a possible precursor of benzoic acid (25a), during workup, through its interaction with oxygen. This fact is further confirmed by the observation that the reaction of 10a with potassium in THF, followed by the treatment with moist THF, in a separate experiment, gave a mixture of benzyl alcohol (23a, 46%) and benzoic acid (25a, 41%). In contrast, the reaction of benzaldehyde (10a) with potassium in THF, followed by the usual workup procedure, as employed in the case of nitrones 1a-d, gave a 75% yield of benzoic acid (25a). It is, therefore, to be inferred that under the conditions of workup, which involves exposure of the reaction mixture from benzaldehyde (10a) (or the nitrone 1a) to air, most of the dianion 20 is converted to the hydroperoxy anion intermediate 21 and ultimately to 25a. This is further substantiated by the observation that the reaction of

10a with potassium in THF, saturated with oxygen, gave a 77% yield of 25a.

When the reaction mixture from 1a (after treatment with potassium in THF) was treated with benzoyl chloride, a mixture of trans-stilbene (13a, 6%), trans-azobenzene (19a, 75%), benzaldehyde (10a, 39%), benzoic acid (25a, 5%), benzoic anhydride (24, 50%) and benzanilide (9, 17%) was obtained. The formation of 24 in this reaction can be explained in terms of the reaction of the intermediates 20 and 21 with benzoyl chloride. In support of this view, it has been observed that treatment of the reaction mixture, obtained from the reaction of benzaldehyde (10a) with potassium in THF, with benzoyl chloride, in a separate experiment, gave a 81% yield of benzoic anhydride (24). The fact that some benzaldehyde (10a) could be isolated from the reaction of 1a with potassium in THF, followed by treatment with benzoyl chloride, would suggest that all of 10a is not converted to 20 and ultimately to other products, under our reaction conditions. The formation of small amounts of benzanilide (9) in this reaction, however, can be rationalized in terms of the reaction of dianion intermediate 8 with benzoyl chloride. This would suggest that in the reaction of 1a with potassium in THF, at least part of the reaction proceeds through the intermediates 6, 7 and 8 (Scheme I.1).

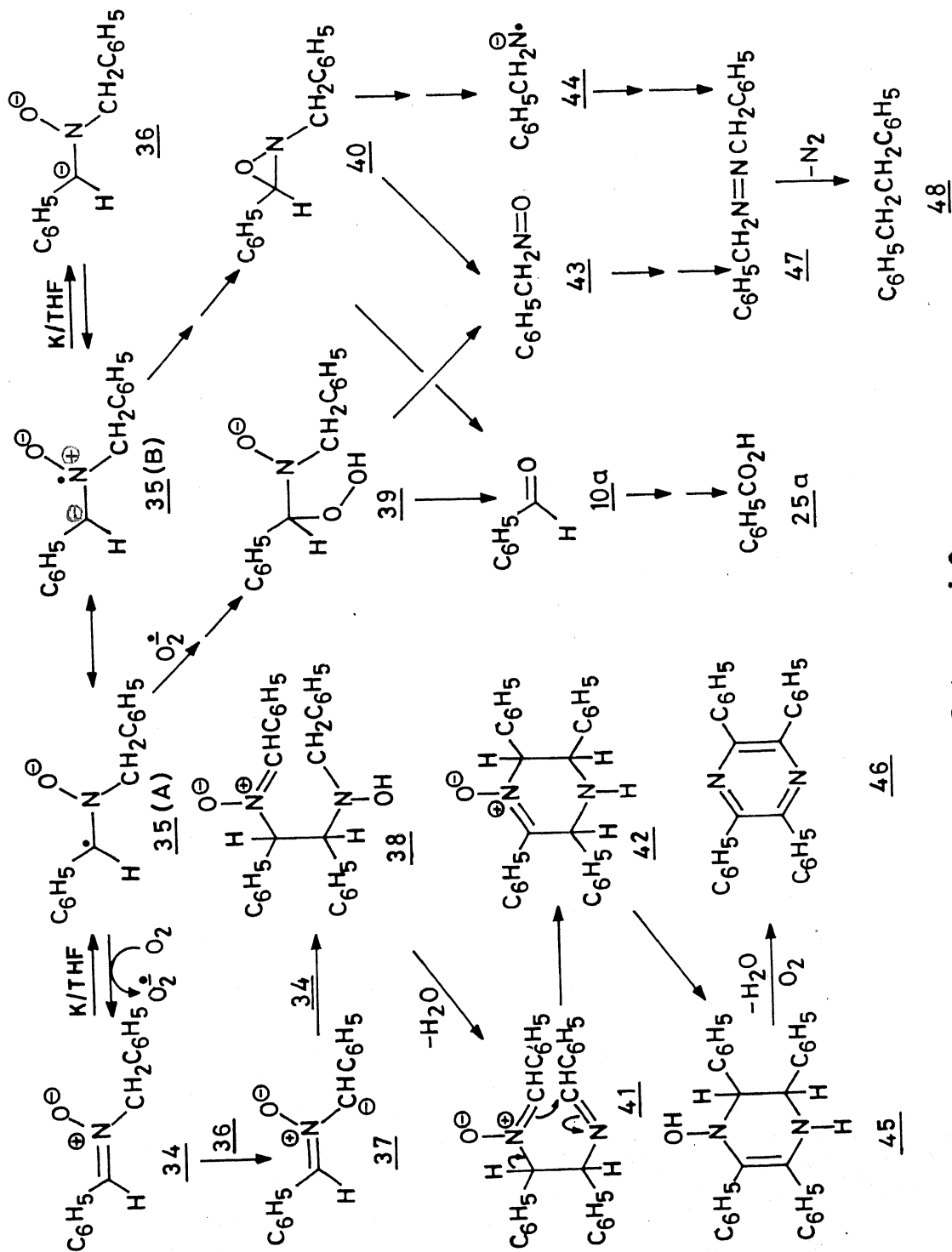
In contrast to the reactions of aldehydonitrones (1a-d), the ketonitrones 26a,b with potassium gave mostly the deoxyge-

nated products 31a and 31b, respectively. It is evident that in these reactions, the pathway involving the dianion intermediates 28a,b is followed. These dianions, under the conditions of work-up could be converted to the N-hydroxy derivatives 30a,b, which will then undergo dehydration to give the Schiff bases 31a,b (Scheme I.2). This difference in behaviour between the aldehydonitrones (1a-d) and ketonitrones (26a,b) could in part be due to the greater stability of the dianions 28a,b and also due to the difficulty of forming oxaziridines from the radical anions 27a,b. It may be indicated that in the reaction of α -diphenylene-N-phenylnitronone (26b) with potassium in THF, saturated with oxygen, under conditions analogous to those of the aldehydonitrones 1(a-d), only a small amount of fluorenone (29b, 28%) could be isolated; nearly 65% of the unchanged starting material (26b) could be recovered from this reaction. However, when the reaction of 26b was carried out in the presence of potassium superoxide and 18-crown-6 in benzene, for a long period of time, fluorenone (29b) could be obtained in better yields. Thus, the treatment of 26b with excess of potassium superoxide (six equivalents) in benzene, containing 18-crown-6 for 42 h at room temperature gave a 72% yield of 29b and a 24% yield of nitrobenzene (22a), in addition to the recovery of a small amount (19%) of the starting material (26b).

The formation of a small amount of 9-anilino fluorene (33b, 8%) besides the major product 31b (71%) in the reaction of 26b with

excess of potassium could be understood in terms of the further reaction of 31b with potassium to give the corresponding dianion intermediate 32b, which under the conditions of workup will lead to 33b. In support of this view, it has been observed that treatment of 31b with potassium in THF, under analogous conditions gave a 73% yield of 9-anilino fluorene (33b), along with a 10% recovery of the starting material, 26b.

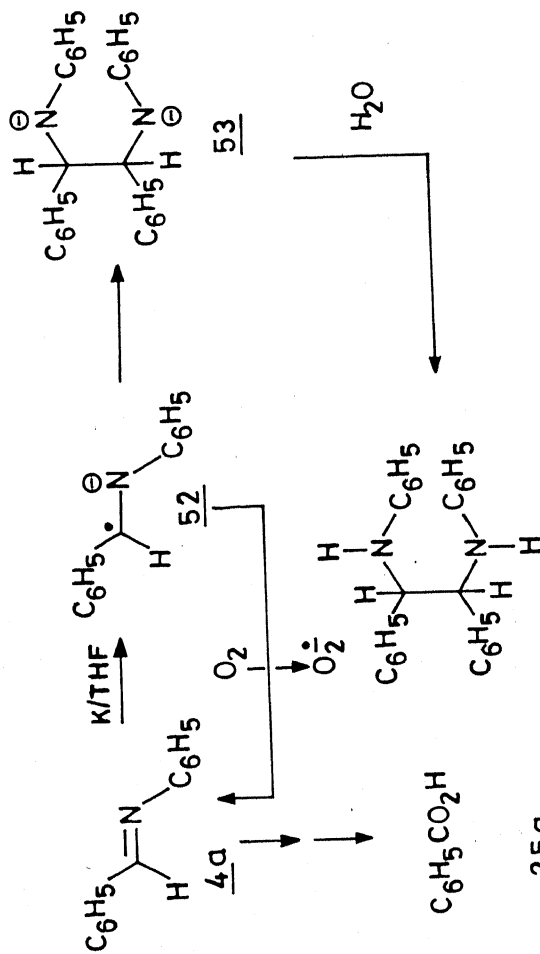
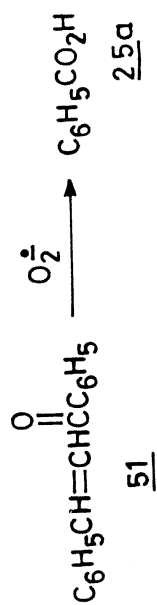
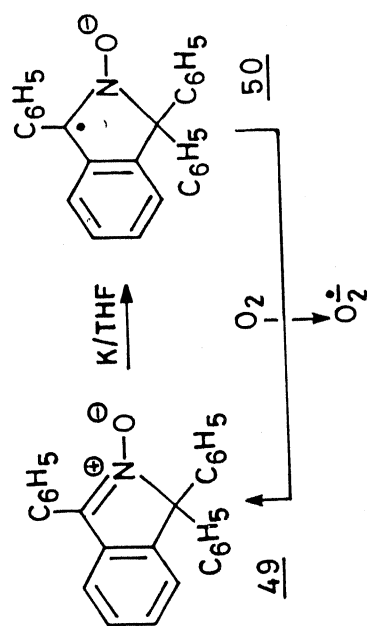
The formation of the different products such as benzoic acid (25a), dibenzyl (48), the nitron 38 and tetraphenylpyrazine (46) in the reaction of 34 with potassium in THF could be understood in terms of the reaction pathway shown in Scheme I.3. The oxaziridine 40 formed from the radical anion intermediate 35 could fragment to benzaldehyde (10a) and the nitroso compound 43. Further reaction of 10a will lead to benzoic acid (25a), whereas the subsequent reaction of 43 with potassium could give the corresponding azo compound 47. Loss of nitrogen from either 47 or one of its precursors involving intermediates 40 and 44 could give dibenzyl (48). The formation of the nitron 38 and tetraphenylpyrazine (46), however, could be rationalized in terms of the anionic intermediate 37, which may be formed through the abstraction of one of the benzylic protons by superoxide or any other base (36). This anionic species 37 can combine with the starting nitron 34 to give 38. In this connection, it may be pointed out that 38 has been reported to be formed in moderate yields, on treatment of 34 with lithium dimethylsilylate.¹³ Subsequent



Scheme 1.3

transformations of 38, involving the loss of two molecules of water and air-oxidation will ultimately give 46, as shown in Scheme I.3.

In contrast to the reactions of the aldehydonitrones 1a-d and ketonitrones 26a,b, the reaction of 1,1,3-triphenylisoindole N-oxide (49) with potassium in THF did not give rise to any product. It is assumed that 49 initially accepts an electron from potassium to give the radical anion intermediate 50 (as evidenced by colour changes), which then reverts back to the starting material (49), on exposure to air, under workup conditions. To substantiate this view, in a separate experiment, oxygen gas was bubbled through the reaction mixture obtained by the treatment of the N-oxide 49 with potassium in THF and subsequently treated this mixture with benzalacetophenone (51) to give a 70% yield of benzoic acid (25a) and 69% yield of the unchanged starting material (49). This clearly shows that superoxide, generated on reaction of 50 with oxygen, reacts with 51 to give benzoic acid (25a). Mention may be made in this connection that 51 is known to undergo oxidation with potassium superoxide to give benzoic acid.¹⁴ The absence of any reaction product, other than the generation of 50, in the reaction of 49 with potassium would imply the non-reactivity of superoxide with the starting N-oxide (49). This is supported by the observation that the reaction of 49 with potassium superoxide in benzene, in the presence of 18-crown-6, under conditions analogous to the oxidation of 1a



Scheme 1.4

and 26b, did not give any isolable product; most of the starting material (49, 69%) was recovered unchanged (Scheme I.4).

I.4 CYCLIC VOLTAMMETRIC STUDIES¹⁵

It has been reported earlier that aromatic amine N-oxides undergo electrochemical reduction to give the corresponding radical anions.^{16,17} To examine whether the radical anions 2a-d, 27a,b, 35 and 50 and the dianions 3a-d, 28a,b and 36 are actually involved in the reaction of the starting nitrones 1a-d, 26a,b, 34 and 49 with potassium, an attempt was made to generate these reactive intermediates electrochemically and to characterize them through their reduction potentials and electronic spectra. In this connection, we have recorded the cyclic voltammograms of the nitrones 1a-d, 26a,b, 34 and 49 and Figure I.1 shows the cyclic voltammograms of three representative nitrones such as 1a, 34 and 49. The values for the peak potential for the one electron (E_p^1) and two electron (E_p^2) reductions for these quasi-reversible systems were evaluated and are listed in Table I.1. It is pertinent to observe that in the cathodic sweep cyclic voltammograms of all the nitrones except 49, the backward sweep waves, which should correspond to the oxidation of the dianions and the radical anions were not observed. In the case of 49, however, the backward sweep corresponding to the one electron redox system could be observed, suggesting thereby that the formation of the radical anion 50 and its oxidation are fully reversible.

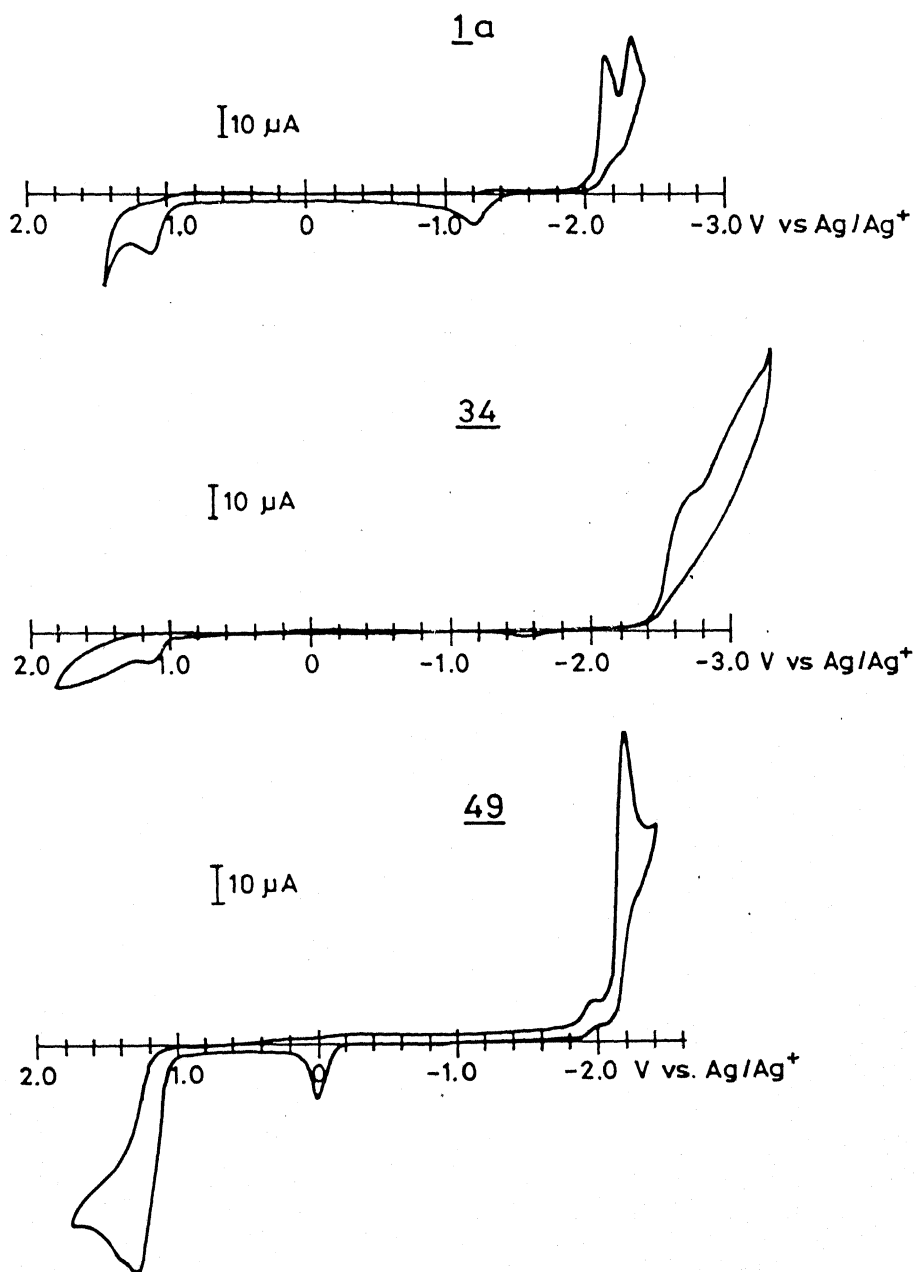


Figure I.1 Cyclic voltammograms of 1a, 34 and 49

reduction peak potentials and spectral data of nitrones, their radical anions and dianions

Compound	Reduction		Nitron		Absorption maxima			
	E_p^1 V vs. Ag/Ag ⁺	E_p^2	λ_{max} nm	ϵ $\times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	Radical anion ^a		Dianion ^a	
					λ_{max}^b nm	λ_{max}^c $\times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	λ_{max}^c nm	$\epsilon^{c,d}$ $\times 10^3 \text{ M}^{-1} \text{ s}^{-1}$
<u>1a</u>	-2.15	-2.35	316	26.5	360, 385	390	290	8.6
<u>1b</u>	-1.90	-2.68	300	13.0	390, 450	450	290	16.5
<u>1c</u>	-2.30	-2.52	320	27.0	370, 390	380	280	21.0
<u>1d</u>	-2.28	-2.55	316	20.0	360, 385	380	295	5.0
<u>26a</u>	-2.13	-2.38	312	14.5	376, 400	e	290	14.5
<u>26b</u>	-1.75	-1.90	353	30.0	400, 550	400	283	30.0
<u>34</u>	-2.70	-3.15	298	16.0	360	380	291	30.0
<u>49</u>	-2.05	-2.30	340	8.0	330	e	292	8.0

a, Both radical anions and dianions were stable under nitrogen atmosphere during the recording of the spectra.

b, Measured from pulse radiolysis experiments (solvent methanol).

c, Measured from electrochemical experiments (solvent acetonitrile, 0.1 M TBAP).

d, At the absorption maximum (error \pm 25%).

e, Measurements could not be made due to the absorption of the starting nitron.

To characterize the radical anions and dianions generated from the nitrones 1a-d, 26a,b, 34 and 49, these substrates were electrochemically reduced in acetonitrile in a specially designed cell, applying the requisite potentials in each case and recorded their electronic spectra. The spectral details are summarized in Table I.1. Examination of Table I.1 reveals that the starting nitrones are characterized by an absorption maximum around 298-353 nm, whereas the corresponding radical anions showed a red shifted absorption maximum around 320-450 nm; the corresponding dianions, however, showed an absorption maximum around 280-295 nm. These observations are in tune with the spectral data reported for radical anions and dianions derived from azobenzene and nitroaromatics through their reaction with lithium in THF.¹⁸⁻²⁰ An interesting observation was that the radical anions 2a-d, 27a,b, 35 and 50 and the dianions 3a-d, 28a,b, and 36 were quenched by oxygen, as evidenced by the disappearance of their absorption bands, on bubbling oxygen gas through their solutions in acetonitrile. It is likely that they react with oxygen to give superoxide anion.

I.5 PULSE RADIOLYSIS STUDIES²¹

Earlier studies on pulse radiolysis of unsaturated substrates, have shown that radical anions can be generated through the attachment of the solvated e^-_{sol} in polar solvents such as methanol under pulse radiolysis conditions.²² In the present

studies, we have observed that the nitrones 1a-d, 26a,b, 34 and 49, undergo electron attachment in methanol to give the corresponding radical anions 2a-d, 27a,b, 35 and 50, respectively, characterized through their absorption spectra (Figure I.2). These radical anions showed strong absorption maxima in the 320-450 nm region, similar to the transients formed under electrochemical conditions and were quenched by oxygen, as proved by their enhanced decay at higher concentrations of oxygen. The close similarity in the spectra of these intermediates, generated under both electrochemical and pulse radiolysis conditions, justifies the assumption that radical anions are the primary intermediates formed through electron transfer process in the reaction of nitrones with potassium.

I.6 EXPERIMENTAL

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The electronic spectra were recorded on a Cary 219 spectrophotometer.

1.6.1 Starting Materials. α ,N-Diphenylnitrone (1a),²³ mp 112-113 °C, α -o-hydroxyphenyl-N-phenylnitrone (1b),²⁴ mp 115 °C, N-phenyl- α -p-tolylnitrone (1c),²⁵ mp 92-93 °C, α -phenyl-N-p-tolylnitrone (1d),⁶ mp 123 °C, triphenylnitrone (26a),³ mp 217-218 °C, α -diphenylene-N-phenylnitrone (26b),²⁶ mp 191-192 °C, N-benzyl- α -phenylnitrone (34),²⁷ mp 82-83 °C, 1,1,3-triphenylisoindole N-oxide (49),²⁸ mp 198 °C, N-benzylideneaniline (4a),²⁹ mp 89 °C

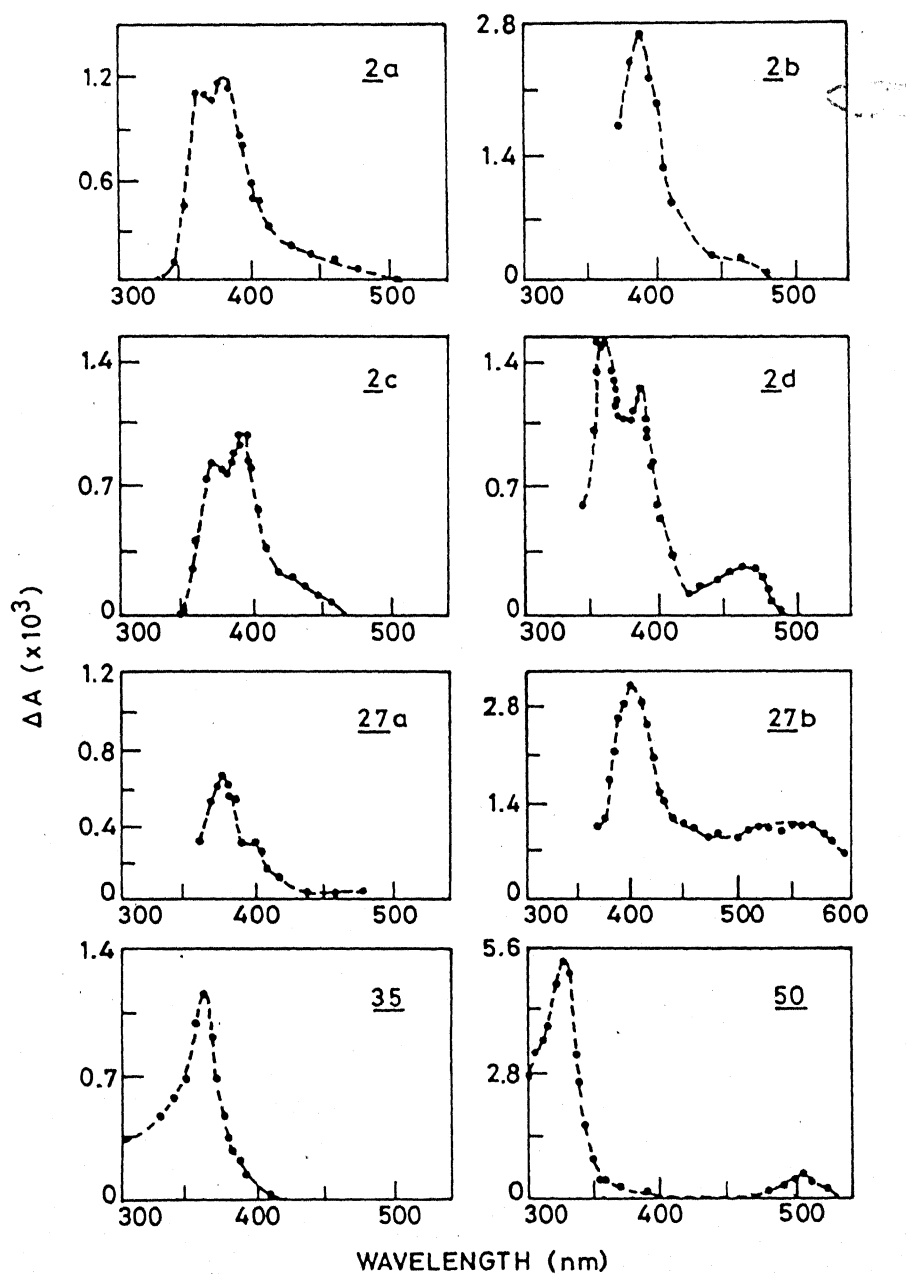


Figure I.2 Absorption spectra of the radical anions 2a-d, 27a,b, 35 and 50

and 9-fluorenylideneaniline (31b), ³⁰ mp 89 °C were prepared by reported procedures. Petroleum ether was the fraction with bp 60-80 °C. Gold Label acetonitrile was used for cyclic voltammetric studies.

1.6.2 Reaction of Nitrones 1a-d, 26a,b, 34, and 49 with Potassium in THF. A general procedure was to shake a mixture of the appropriate nitrone (1a-d, 26a,b, 34, 49) and excess of finely cut potassium in THF (125 mL) in a stoppered round bottomed flask for several hours. A few clean, broken glass pieces were added to the mixture to ensure a fresh surface of metal throughout the reaction. In general, the reaction mixture underwent pronounced colour changes due to the formation of radical anion and dianion intermediates. On completion of the reaction, the mixture was poured into moist THF (100 mL) to destroy any unchanged potassium and then the solvent was removed under vacuum to give a residual solid. This material was treated with water (10 mL) and extracted with methylene chloride (100 mL). Acidification of the aqueous layer with dilute hydrochloric acid and extraction with methylene chloride (100 mL) gave the carboxylic acid fraction, which was crystallized from suitable solvents.

Workup of the non-aqueous fraction (methylene chloride extract), by removal of solvent under vacuum and by fractional crystallization from suitable solvents or by chromatographing over alumina gave the non-acidic products.

I.6.3 Reaction of α ,N-Diphenylnitron (1a) with Potassium in THF. Treatment of 590 mg (3 mmol) of 1a with potassium (235 mg, 6 mg-atom) in THF for 16 h and workup in the general manner gave 170 mg (47%) of benzoic acid (25a), mp 121 °C (mixture mp). The non-aqueous fraction (methylene chloride extract) was worked up by removal of the solvent under vacuum and chromatographing over alumina. Elution with petroleum ether gave 20 mg (8%) of trans-stilbene (13a), mp 124 °C (mixture mp). Further elution with a mixture (1:4) of benzene and petroleum ether gave 220 mg (82%) of trans-azobenzene (19a) mp 68 °C (mixture mp). Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 130 mg (42%) of benzaldehyde (10a) (superimposable ir spectrum with that of an authentic sample).

In a repeat run, 1a (590 mg, 3 mmol) was treated with potassium (235 mg, 6 mg-atom) in THF (125 mL), saturated with oxygen, for 16 h. Workup as in the earlier case gave 170 mg (47%) of benzoic acid (25a), mp 121 °C (mixture mp), from the aqueous fraction. The non-aqueous fraction was chromatographed over alumina and eluted with petroleum ether to give 20 mg (8%) of 13a, mp 124 °C (mixture mp). Further elution with a mixture (1:9) of benzene and petroleum ether gave 260 mg (70%) of nitrobenzene (22a) (superimposable ir spectrum with that of an authentic sample). Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 120 mg (38%) of benzaldehyde (10a) (superimposable ir spectrum with that of an authentic sample).

In yet another run, 1a (590 mg, 3 mmol) was treated with potassium (235 mg, 6 mg-atom) in THF for 16 h. Moist THF (25 mL) was injected into the reaction mixture and the shaking was continued for an additional 5 h. Workup of the reaction mixture as in the earlier cases gave 90 mg (25%) of benzoic acid (25a), mp 121 °C (mixture mp), 20 mg (7%) of trans-stilbene (13a), mp 124 °C (mixture mp), 210 mg (78%) of trans-azobenzene (19a), mp 68 °C (mixture mp), 80 mg (25%) of benzyl alcohol (23a) (superimposable ir spectrum with that of an authentic sample) and 100 mg (32%) of benzaldehyde (10a) (superimposable ir spectrum with that of an authentic sample).

In another run, 1a (590 mg, 3 mmol) was treated with potassium (235 mg, 6 mg-atom) in THF (125 mL) for 16 h. A solution of benzoyl chloride (425 mg, 3 mmol) in THF (25 mL) was injected into the reaction vessel and the shaking was continued for an additional 5 h. Workup of the mixture in the usual manner gave 18 mg (5%) of benzoic acid (25a), mp 121 °C (mixture mp), from the aqueous fraction. The non-aqueous fraction was chromatographed over alumina. Elution with petroleum ether gave 15 mg (6%) of trans-stilbene (13a), mp 124 °C (mixture mp). Further elution with a mixture (1:9) of benzene and petroleum ether gave 200 mg (75%) of trans-azobenzene (19a), mp 68 °C (mixture mp). Subsequent elution with a mixture (3:7) of benzene and petroleum ether gave 330 mg (50%) of benzoic anhydride (24), mp 42 °C (mixture mp). Elution with a mixture (1:1) of benzene and petroleum ether gave 123 mg (39%) of benzaldehyde (10a) (superimposable ir spectrum

with that of an authentic sample) and finally elution with benzene gave 100 mg (17%) of benzanilide (9), mp 163-164 °C (mixture mp).

1.6.4 Reaction of Benzaldehyde (10a) with Potassium in THF. Treatment of 10a (636 mg, 6 mmol) with potassium (235 mg, 6 mg-atom) in THF (125 mL) for 15 h and workup in the usual manner gave 550 mg (75%) of benzoic acid (25a), mp 121 °C (mixture mp).

In a repeat run, 10a (636 mg, 6 mmol) was treated with potassium (235 mg, 6 mg-atom) in THF (125 mL), saturated with oxygen. Workup of the mixture as in the earlier cases gave 565 mg (77%) of 25a, mp 121 °C (mixture mp).

In yet another run, 10a (636 mg, 6 mmol) was treated with potassium (235 mg, 6 mg-atom) in THF (125 mL) for 15 h. Moist THF (25 mL) was injected into the reaction vessel and the shaking was continued for an additional 5 h. Workup as in the earlier cases gave 300 mg (41%) of 25a, mp 121 °C (mixture mp) and 300 mg (46%) of benzyl alcohol (23a) (superimposable ir spectrum with that of an authentic sample).

In a repeat run, 10a (636 mg, 6 mmol) was treated with potassium (235 mg, 6 mg-atom) in THF (125 mL) for 15 h. A solution of freshly distilled benzoyl chloride (840 mg, 6 mmol) in THF (25 mL) was injected into the reaction vessel and the shaking was continued for an additional 5 h. Workup in the usual manner gave 1.1 g (81%) of benzoic anhydride (24), mp 42 °C (mixture mp).

1.6.5 Reaction of α -o-Hydroxyphenyl-N-phenylnitrone (1b) with Potassium in THF. Treatment of 640 mg (3 mmol) of 1b with potassium (235 mg, 6 mg-atom) in THF (125 mL) for 10 h and work-up in the usual manner gave 125 mg (30%) of salicylic acid (25b), mp 159 °C (mixture mp), from the aqueous fraction. Workup of the non-aqueous fraction gave a residual solid, which was chromatographed over alumina. Elution with petroleum ether gave 160 mg (58%) of trans-azobenzene (19a), mp 68 °C (mixture mp), after recrystallization from ethanol. Further elution with a mixture (1:1) of benzene and petroleum ether gave 90 mg (25%) of salicylaldehyde (10b) (superimposable ir spectrum with that of an authentic sample). Subsequent elution with a mixture (4:3) of benzene and petroleum ether gave 130 mg (20%) of the unchanged starting material (1b), mp 118 °C (mixture mp), after recrystallization from benzene.

In a repeat run, 640 mg (3 mmol) of 1b was treated with 470 mg (12 mg-atom) of potassium in THF (125 mL) for 15 h and worked up as in the earlier cases to give 185 mg (45%) of 25b, mp 159 °C (mixture mp), 190 mg (69%) of 19a, mp 68 °C (mixture mp) and 135 mg (37%) of 10b (superimposable ir spectrum with that of an authentic sample).

1.6.6 Reaction of N-Phenyl- α -p-tolylnitrone (1c) with Potassium in THF. A solution of 1c (640 mg, 3 mmol) in THF (125 mL) was shaken with potassium (235 mg, 6 mg-atom) for 15 h. The colourless solution became yellow, at first, later brown and

finally black. Workup of the mixture as in the earlier cases gave 180 mg (44%) of p-toluic acid (25c), mp 182 °C (mixture mp), after recrystallization from benzene. Workup of the non-aqueous fraction gave a residual solid, which was chromatographed over alumina. Elution with petroleum ether gave 20 mg (6%) of trans-1,2-di-p-tolyl-ethylene (13c), mp 179 °C (mixture mp).³¹ Further elution with a mixture (1:9) of benzene and petroleum ether gave 220 mg (80%) of trans-azobenzene (19a), mp 68 °C (mixture mp), after recrystallization from ethanol. Elution with a mixture (1:1) of benzene and petroleum ether gave 145 mg (40%) of p-tolualdehyde (10c) (superimposable ir spectrum with that of an authentic sample).

I.6.7 Reaction of α -Phenyl-N-p-tolylnitron (1d) with Potassium in THF. A solution of 1d (640 mg, 3 mmol) in THF (125 mL) was shaken with potassium (235 mg, 6 mg-atom) for 12 h. Workup of the mixture as in the earlier cases gave 180 mg (49%) of benzoic acid (25a), mp 121 °C (mixture mp). The non-aqueous fraction was chromatographed over alumina and eluted with petroleum ether to give 10 mg (4%) of trans-stilbene (13a), mp 124 °C (mixture mp). Further elution with a mixture (1:9) of benzene and petroleum ether gave 280 mg (89%) of trans-p-azotoluene (19d), mp 144 °C (mixture mp), after recrystallization from ethanol. Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 130 mg (40%) of benzaldehyde (10a) (superimposable ir spectrum with that of an authentic sample).

I.6.8 Reaction of Triphenylnitrone (26a) with Potassium in THF. Treatment of 26a (1.37 g, 5 mmol) with potassium (390 mg, 10 mg-atom) in THF for 3.5 h and workup as in the earlier cases gave 1.05 g (82%) of benzophenone anil (31a), mp 113-114 °C (mixture mp), after recrystallization from methanol. Workup of the aqueous fraction in the usual manner did not give any isolable product.

I.6.9 Reaction of α -Diphenylene-N-phenylnitrone (26b) with Potassium in THF. Treatment of 26b (1.08 g, 4 mmol) with potassium (315 mg, 8 mg-atom) in THF for 10 h and workup as in the earlier cases gave 820 mg (81%) of 9-fluorenylideneaniline (31b), mp 89 °C (mixture mp), after recrystallization from a mixture (1:3) of chloroform and ethanol.

In a repeat run, 1.36 g (5 mmol) of 26b was treated with excess of potassium (780 mg, 20 mg-atom) in THF for 10 h, under analogous conditions and worked up to give 100 mg (8%) of 9-anilino-fluorene (33b), mp 123-124 °C (mixture mp)³² and 900 mg (71%) of 9-fluorenylideneaniline (31b), mp 89 °C (mixture mp).

In yet another run, 26b (108 mg, 0.4 mmol) was treated with potassium (30 mg, 0.8 mg-atom) for 10 h in THF (125 mL), which was previously saturated with oxygen. Workup of the reaction mixture as in the earlier cases gave 20 mg (28%) of 29b, mp 84 °C (mixture mp) and 70 mg (65%) of the unchanged starting material (26b), mp 191-192 °C (mixture mp).

I.6.10 Reaction of N-benzyl- α -phenylnitrone (34) with Potassium in THF. A solution of 34 (950 mg, 4.5 mmol) in THF (125 mL) was shaken with potassium (180 mg, 4.5 mg-atom) for 10 h. The solution, which was colourless initially changed to yellow, red and finally brown. The reaction mixture was poured into moist THF (100 mL) and then removed the solvent under vacuum. The residual solid thus obtained was treated with water (10 mL) and extracted with methylene chloride. The aqueous layer on acidification with dilute hydrochloric acid and extraction with methylene chloride gave 100 mg (18%) of 25a, mp 121 °C (mixture mp). Removal of the solvent from the earlier methylene chloride extract gave a product mixture, which was chromatographed over alumina. Elution with petroleum ether gave 75 mg (18%) of dibenzyl (48), mp 52 °C (mixture mp).³³ Further elution with a mixture (1:4) of benzene and petroleum ether gave 150 mg (17%) of 2,3,5,6-tetraphenylpyrazine (46), mp 249 °C (mixture mp).¹³ Further elution of the column with a mixture (2:3) of benzene and petroleum ether gave 200 mg (21%) of α -phenyl-N-(2-benzylhydroxyamino-1,2-diphenylethano)nitrone (38), mp 196 °C (mixture mp).¹³ Subsequent elution with benzene gave 75 mg (8%) of the unchanged starting material (34), mp 82-83 °C (mixture mp).

I.6.11 Reaction of 1,1,3-Triphenylisoindole N-oxide (49) with Potassium in THF. A solution of 49 (360 mg, 1 mmol) in THF (125 mL) was shaken with potassium (78 mg, 2 mg-atom) for 12 h. The solution which was initially colourless changed to yellow and

finally to orange. Exposure of the reaction mixture to air destroyed the colour. Workup of the reaction mixture as in the usual manner gave 250 mg (69%) of the unchanged starting material (49), mp 198 °C (mixture mp), as the only isolable product.

In a repeat run, 360 mg (1 mmol) of 49 was treated with 78 mg (2 mg-atom) of potassium in THF (125 mL) for 12 h. Oxygen gas was bubbled through the reaction mixture and afterwards a solution of benzalacetophenone (51) (210 mg, 1 mmol) in benzene (25 mL) was added to the mixture and was shaken for a further period of 2 h. Workup of the reaction mixture as in the earlier cases gave 250 mg (69%) of the unchanged nitron (49), mp 198 °C (mixture mp) and 170 mg (70%) of benzoic acid (25a), mp 121 °C (mixture mp).

I.6.12 Reaction of N-Benzylideneaniline (4a) with Potassium in THF. A solution of 4a (1.36 g, 7.5 mmol) in THF (125 mL) was shaken with potassium (1.17 g, 30 mg-atom) for 9 h. The solution which was initially colourless became yellow, then brown and finally colourless again. Workup in the usual manner gave 260 mg (28%) of benzoic acid (25a), mp 121 °C (mixture mp), after recrystallization from hot water and 760 mg (55%) of d,l-N,N',1,2-tetraphenylethylenediamine (54), mp 150-151 °C (mixture mp),³⁴ after recrystallization from ethanol.

I.6.13 Reaction of 9-Fluorenylideneaniline (31b) with Potassium in THF. A solution of 31b (1.02 g, 4 mmol) in THF

(125 mL) was shaken with potassium (315 mg, 8 mg-atom) for 10 h. The reaction mixture was treated with moist THF (10 mL) and later, the solvent was removed under vacuum. The residual solid was extracted with ether to give a product mixture, which was then triturated with ethanol (2 mL). The ethanol-insoluble fraction gave 750 mg (73%) of 9-anilino fluorene (33b), mp 124 °C (mixture mp), after recrystallization from ethanol. The ethanol-soluble fraction was evaporated under vacuum to give 100 mg (10%) of the unchanged starting material (31b), mp 89 °C (mixture mp), after recrystallization from a mixture (1:3) of chloroform and ethanol.

I.6.14 Reaction of α ,N-Diphenylnitrone (1a) with Potassium Superoxide. A mixture of 1a (390 mg, 1.98 mmol), potassium superoxide (290 mg, 4 mmol) and 18-crown-6 (530 mg, 2 mmol) in benzene (100 mL) was stirred at room temperature for 24 h, protected from sunlight. The reaction mixture became yellow at first and later turned orange and finally red. On completion of the reaction, the mixture was washed several times with aqueous sodium chloride solution. Removal of the solvent from the organic layer under vacuum gave 220 mg (89%) of nitrobenzene (22a) (superimposable ir spectrum with that of an authentic sample).

The combined aqueous washings were acidified with dilute hydrochloric acid and extracted with benzene. Removal of the solvent from the benzene extract under vacuum gave 200 mg (82%) of benzoic acid (25a), mp 121 °C (mixture mp).

I.6.15 Reaction of α -Diphenylene-N-phenylnitrone (26a) with Potassium Superoxide. A mixture of 26b (270 mg, 1 mmol), potassium superoxide (420 mg, 6 mmol) and 18-crown-6 (530 mg, 2 mmol) in benzene (100 mL) was stirred at room temperature for 42 h, protected from sunlight. The mixture was washed several times with aqueous sodium chloride solution. Removal of the solvent from the organic layer under vacuum gave a product mixture, which was chromatographed over alumina. Elution with petroleum ether gave 30 mg (24%) of nitrobenzene (22a) (superimposable ir spectrum with that of an authentic sample). Elution with a mixture (1:4) of benzene and petroleum ether gave 130 mg (72%) of 9-fluorenone (29b), mp 84 °C (mixture mp). Further elution with a mixture (3:1) of benzene and petroleum ether gave 50 mg (19%) of the unchanged starting material (26b), mp 191-192 °C (mixture mp).

I.6.16 Attempted Reaction of 1,1,3-Triphenylisoindole N-oxide (49) with Potassium Superoxide. A mixture 49 (180 mg, 0.5 mmol), potassium superoxide (70 mg, 1 mmol) and 18-crown-6 (135 mg, 0.5 mmol) in benzene (100 mL) was stirred at room temperature for 12 h, protected from sunlight. Workup of the reaction mixture as in the earlier cases gave 125 mg (69%) of the unchanged starting material (49), mp 198 °C (mixture mp), as the only isolable product.

I.6.17 Reaction of Nitrosobenzene (11a) with Potassium Superoxide. A mixture of 11a (428 mg, 4 mmol), potassium

superoxide (288 mg, 4 mmol) and 18-crown-6 (530 mg, 2 mmol) in benzene (100 mL) was stirred at room temperature for 6 h. Work-up of the reaction mixture as in the earlier cases gave 300 mg (61%) of nitrobenzene (22a) (superimposable ir spectrum with that of an authentic sample).

I.6.18 Cyclic Voltammetry. Cyclic voltammetric measurements were made with a Princeton Applied Research (PAR) Model 173 Potentiostat /Galvanostat, a PAR Model 175 Universal Programmer and a Kipp and Zonen X-Y recorder. Experiments were performed in a standard three compartment cell equipped with a Pt-disc working electrode, Pt-wire counter electrode and Ag/Ag^+ reference electrode. For spectroelectrochemical measurements a specially designed cell was employed, which consists of an extended 10 mm quartz cuvette, equipped with a Pt-gauze working electrode, a Pt-foil counter electrode and an Ag/Ag^+ reference electrode. The electrolysis was carried out in acetonitrile solution (~ 0.05 M), under nitrogen atmosphere at controlled potentials and the absorption spectra of the electrochemically generated radical anions and dianions were recorded directly in a Cary 219 spectrophotometer. Both one electron and two electron reduction processes were monitored directly using a PAR 179 Digital Coulometer.

I.6.19 Pulse Radiolysis. The computer controlled pulse radiolysis apparatus, which allows determination of transient spectra at various times after the pulse and kinetic measurements of the spectral changes have been described earlier elsewhere.³⁵

The solutions of nitrones in methanol (~ 0.5 mM) were deaerated before pulse radiolysis by bubbling nitrogen for at least half an hour. The deaeration was continued in the reservoir from which the solution was allowed to flow slowly and continuously through the pulse radiolysis cell.

The irradiation was carried out with 5 ns electron pulses from the Notre Dame 7 MeV ARCO LP-7 linear accelerator using dose rates of 2×10^{16} eV/g per pulse.

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CHAPTER II

ELECTRON TRANSFER REACTIONS. REACTION OF DIBENZOBARRELENES WITH POTASSIUM

II.1 ABSTRACT

The reaction of several dibenzobarrelenes (1a-f) with potassium in THF has been investigated. Dibenzobarrelenes (1a-f), on treatment with potassium in THF, give rise to radical anions (2, 4) and dianion intermediates (5), through electron transfer reactions, and these intermediates undergo further transformations to give a variety of products. Thus, the dibenzobarrelenes 1a,b,d-f gave the corresponding anthracenes 6a,b,d-f, dihydrodibenzobarrelenes 10a,b,d-f and benzoic acid (8). The dibenzobarrelenes 1a,f gave also the monodebenzoylated products 18a,f, whereas 1d, gave both anthraquinone (25) and the enol derivative 31, besides 6d, 10d and 8. In contrast to the reaction of 1a,b,d-f, 1c gave a mixture of products consisting of benzoic acid (8), anthracene (24), the anthrone 23 and the anthrol 26. In order to assess the involvement of any oxygen in the formation of the different products, the reaction of some representative substrates (1a,c,d) with potassium in THF, saturated with oxygen and with potassium superoxide were studied. Cyclic voltammetric studies have been carried out to measure the reduction potentials for both one electron and two electron processes, leading to the corresponding radical anion and dianion intermediates.

The radical anions of these substrates (1a-f) were also generated pulse radiolytically in methanol and their spectra showed absorption maxima in the regions 310-390 and 400-500 nm. Reasonable mechanisms have been proposed for the formation of the different products in these reactions.

II.2 INTRODUCTION

Several studies concerning the reaction of 1,2-dibenzoylalkenes with different reducing agents have been reported in the literature.¹⁻⁷ The reduction of both cis- and trans-dibenzoylstyrene with zinc and acetic acid, for example, has been shown to give a mixture of 1,2-dibenzoyl-1-phenylethane and 2,3,5-triphenylfuran, in each case.¹ Winecoff et al.⁸ have examined the electrochemical reduction of the geometric isomers of different 1,2-dibenzoylalkenes such as dibenzoylethylene, dibenzoylstyrene and dibenzoylstilbene through polarographic and cyclic voltammetric techniques. They have shown that there is an appreciable difference in the ease of reduction between the cis- and trans-isomers, in each case, and that the reduction becomes more difficult, upon successive introduction of phenyl groups in these substrates.

Only very few examples of the reaction of 1,2-dibenzoylalkenes with alkali metals have been reported so far. The reaction of o-dibenzoylbenzene with alkali metals, for example, has been shown to give different products, depending on the

reaction conditions.⁹⁻¹² Thus, the reaction of o-dibenzoylbenzene with sodium in THF gives a mixture of 1,3-diphenylisobenzofuran, 10-hydroxy-10-phenyl-9-anthrone and a trace of anthraquinone,⁹ whereas the reaction of o-dibenzoylbenzene with potassium is reported to give a dimeric reduction product.¹⁰ Campbell et al.¹¹ have reported that a mixture of 1,3-diphenylisobenzofuran and 10-hydroxy-10-phenyl-9-anthrone is formed, when o-dibenzoylbenzene is treated with potassium in dimethoxyethane.

In a recent investigation,^{13,14} it has been shown that several 1,2-dibenzoylalkenes undergo interesting transformations, on treatment with potassium in THF. Thus, the reaction of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene with potassium, for example, gave a mixture of 2-endo,3-exo-dibenzoylbicyclo[2.2.1]hept-5-ene and 3-(1'-hydroxy-1'-phenylmethylene)bicyclo[2.2.1]hept-2-ene-2-phenyl-2-carboxylic acid and benzoic acid.¹³ Similarly, it has been observed that 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene, on treatment with potassium in THF, gives a mixture of 12-(α -hydroxybenzylidene)-9,10-dihydro-11-phenyl-9,10-ethenoanthracene-11-carboxylic acid, anthracene, and benzoic acid.¹⁴ In this context, it was felt worthwhile to investigate the reaction of some representative dibenzobarrelenes containing 1,2-dibenzoylalkene moieties with potassium in THF, to examine the generality of such reactions.

II.3 RESULTS AND DISCUSSION

The dibenzobarrelenes that we have examined in the present studies include 11,12-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (1a), 11,12-dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-ethenoanthracene (1b), 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (1c), 11,12-dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethenoanthracene (1d), 11,12-dibenzoyl-9,10-dihydro-9-phenyl-9,10-ethenoanthracene (1e) and 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (1f). These substrates (1a-f) were prepared in 72-85% yields through reported procedures, employing the reaction of the appropriate anthracene (6a,b,d-f) or anthrone with dibenzoylacetylene (DBA).

The reaction of 1a with potassium in THF, for example, gave a mixture of 9-methylanthracene (6a, 21%), 12-benzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (18a, 14%), 11-endo, 12-exo-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethanoanthracene (10a, 37%) and benzoic acid (8, 23%). The reaction of 1b, under analogous conditions, gave a mixture of 9-hydroxymethylanthracene (6b, 21%), 11-endo, 12-exo-dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-ethanoanthracene (10b, 32%) and benzoic acid (8, 24%), along with a 18% recovery of the unchanged starting material (1b). In contrast, the reaction of 1c with potassium in THF gave a mixture of anthracene (24, 7%) anthraquinone (25, 7%), 10-(cis-1,2-dibenzoylethenyl)-9-anthrone (23, 21%), 10-(cis-1,2-dibenzoylethenyl)-9-anthrol (26, 31%) and benzoic acid

(8, 14%), whereas 1d, under analogous conditions, gave a mixture of 9-methoxyanthracene (6d, 14%), anthraquinone (25, 17%), 11-endo,12-exo-dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethanoanthracene (10d, 28%), 2-(9-anthracenyl)-1,4-diphenyl-1-hydroxybut-1-ene-3,4-dione (31, 17%) and benzoic acid (8, 26%). The reaction of 1e gave a mixture of 9-phenylanthracene (6e, 15%), 11-endo,12-exo-dibenzoyl-9,10-dihydro-9-phenyl-9,10-ethanoanthracene (10e, 51%), benzoic acid (8, 31%) and some unchanged starting material (1e, 19%). Similarly, the reaction of 1f with potassium in THF gave a mixture of 9,10-dimethylantracene (6f, 15%), 12-benzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (18f, 30%), 11-endo,12-exo-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethanoanthracene (10f, 40%) and benzoic acid (8, 27%). The structures of all the products were established on the basis of analytical results, spectral data and comparison with authentic samples, wherever possible.

The ^1H NMR spectrum of 18a (Figure II.1), for example, showed a singlet at δ 2.33 (3 H), assigned to the methyl protons and a doublet at δ 5.13 ($J_{10,11} = 6$ Hz, 1 H), assigned to the bridgehead proton. It may be pointed out here that similar values for the coupling constant between the bridgehead and vinyl protons ($J_{10,11} = 6$ Hz) in the case of 11-benzoyl-9,10-dihydro-9,10-ethenoanthracene has been reported earlier.¹⁵ The aromatic and vinylic protons in 18a appeared as a complex multiplet centred at δ 7.2 (14 H).

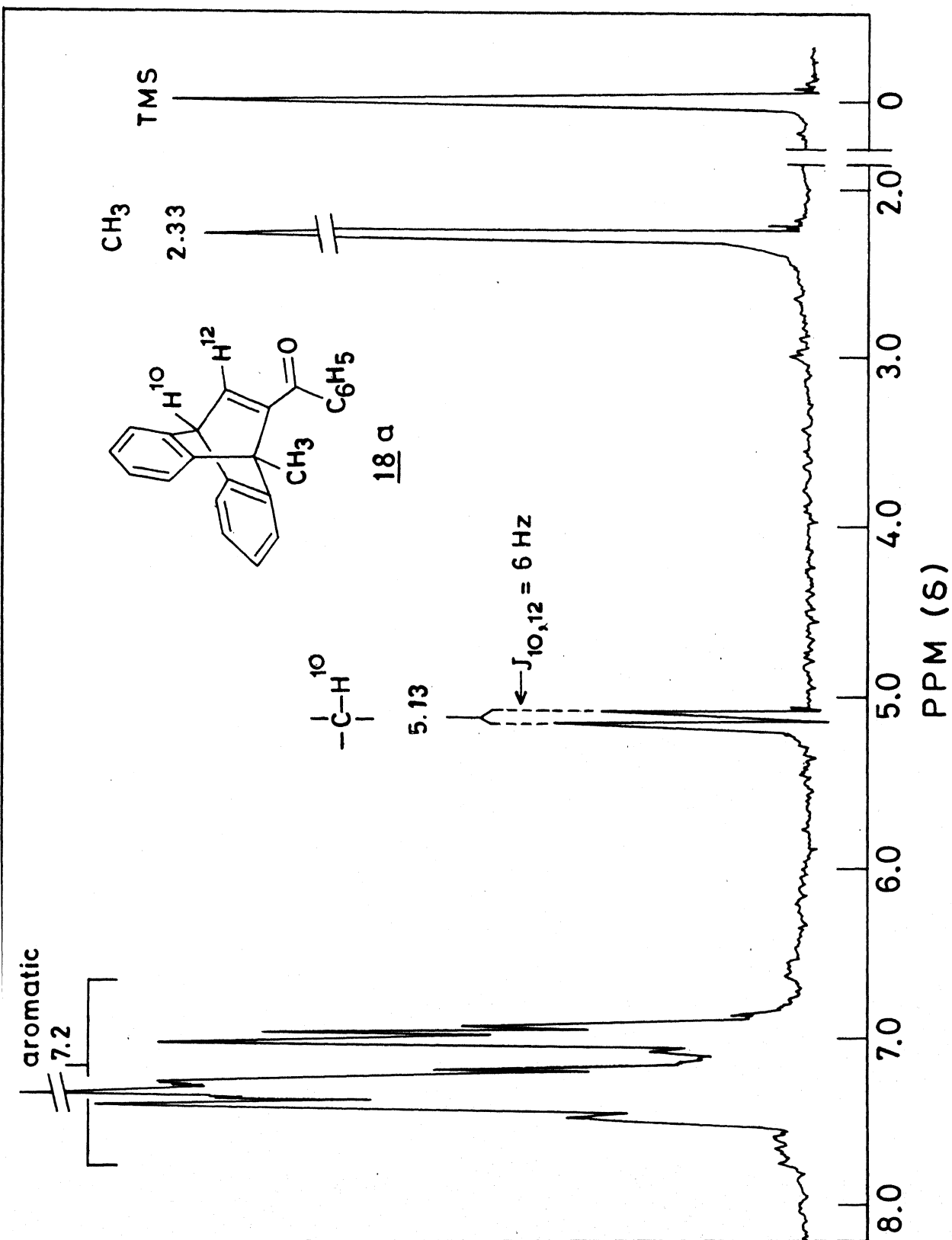
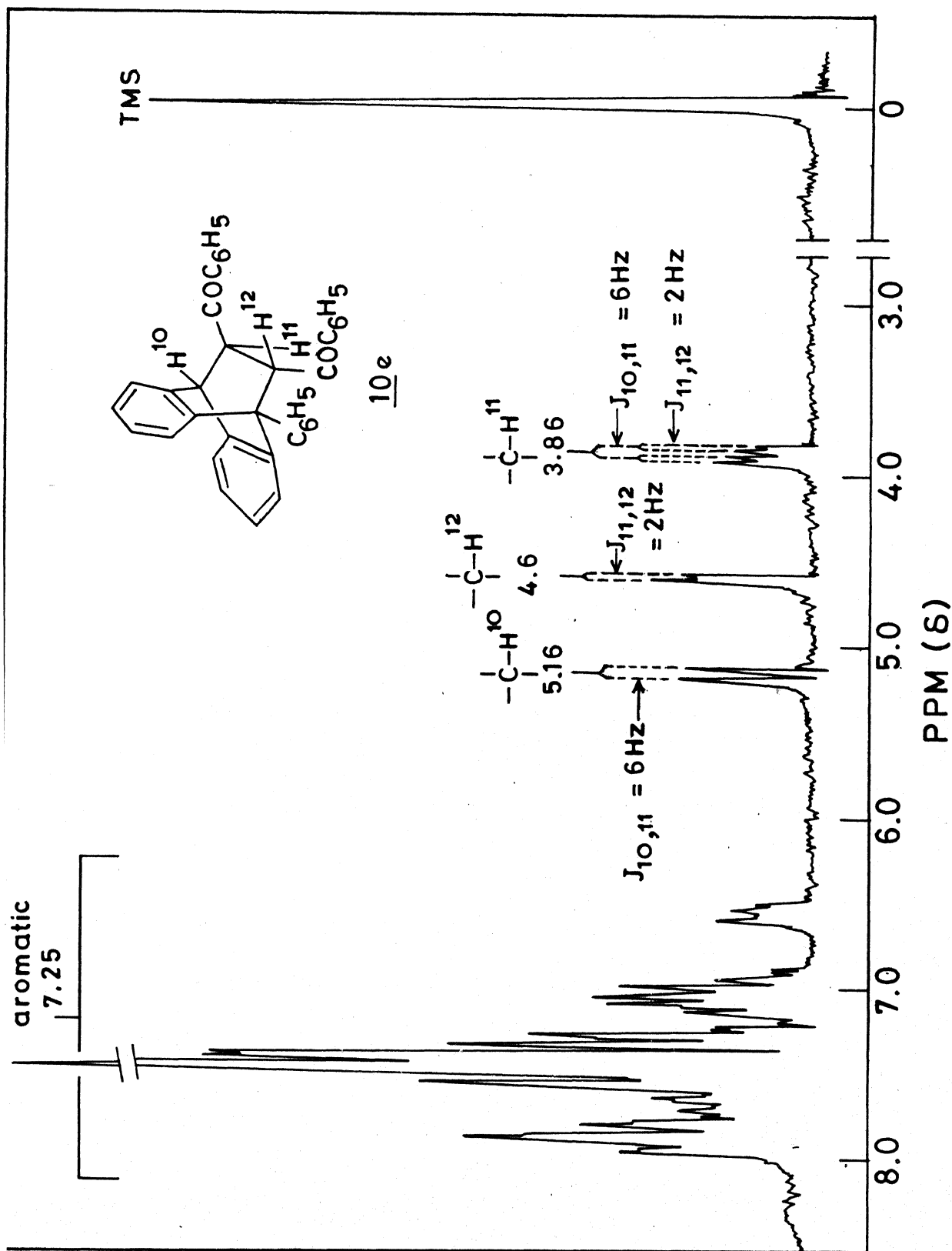


Figure II.1 ^1H NMR spectrum (90 MHz) of **18a**.

The structures of 10a,b,d-f, on the other hand, were confirmed through their independent syntheses, involving the reaction of the appropriate anthracenes (6a,b,d-f) with trans-1,2-dibenzoyl ethylene (DBE). The ^1H NMR spectrum of a representative example, 10e (Figure II.2), for example, showed a doublet of doublets at δ 3.86 ($J_{10,11} = 6$ Hz; $J_{11,12} = 2$ Hz, 1 H), assigned to the H^{11} proton. The doublets at δ 4.6 ($J_{11,12} = 2$ Hz, 1 H) and δ 5.16 ($J_{10,11} = 6$ Hz, 1 H) were assigned to the H^{12} and bridgehead protons, respectively, whereas the aromatic protons appeared as a complex multiplet centred at δ 7.25 (23 H).

The ^1H NMR spectrum of the anthrone 23 (Figure II.3) showed two singlets at δ 5.7 (1 H) and δ 6.7 (1 H), assigned to the methine proton at C^{10} and the vinylic proton, respectively, whereas the aromatic protons appeared as a complex multiplet centred at δ 7.8 (18 H). Similarly, the ^1H NMR spectrum of the anthrol 26 (Figure II.4) showed two singlets at δ 3.65 (1 H, D_2O exchangeable) and δ 6.85 (1 H), assigned to the hydroxyl and vinylic protons, respectively. The aromatic protons appeared as a complex multiplet centred at δ 7.6 (18 H). Further confirmation of the structures of 23 and 26 was derived from the observation that 23 could be transformed to 26, on treatment with sodium hydroxide.

The formation of the different products in the reaction of 1a-f with potassium in THF could be understood in terms of the pathways shown in Schemes II.1-II.4. It has been assumed

Figure II.2 ^1H NMR spectrum (90 MHz) of 10e.

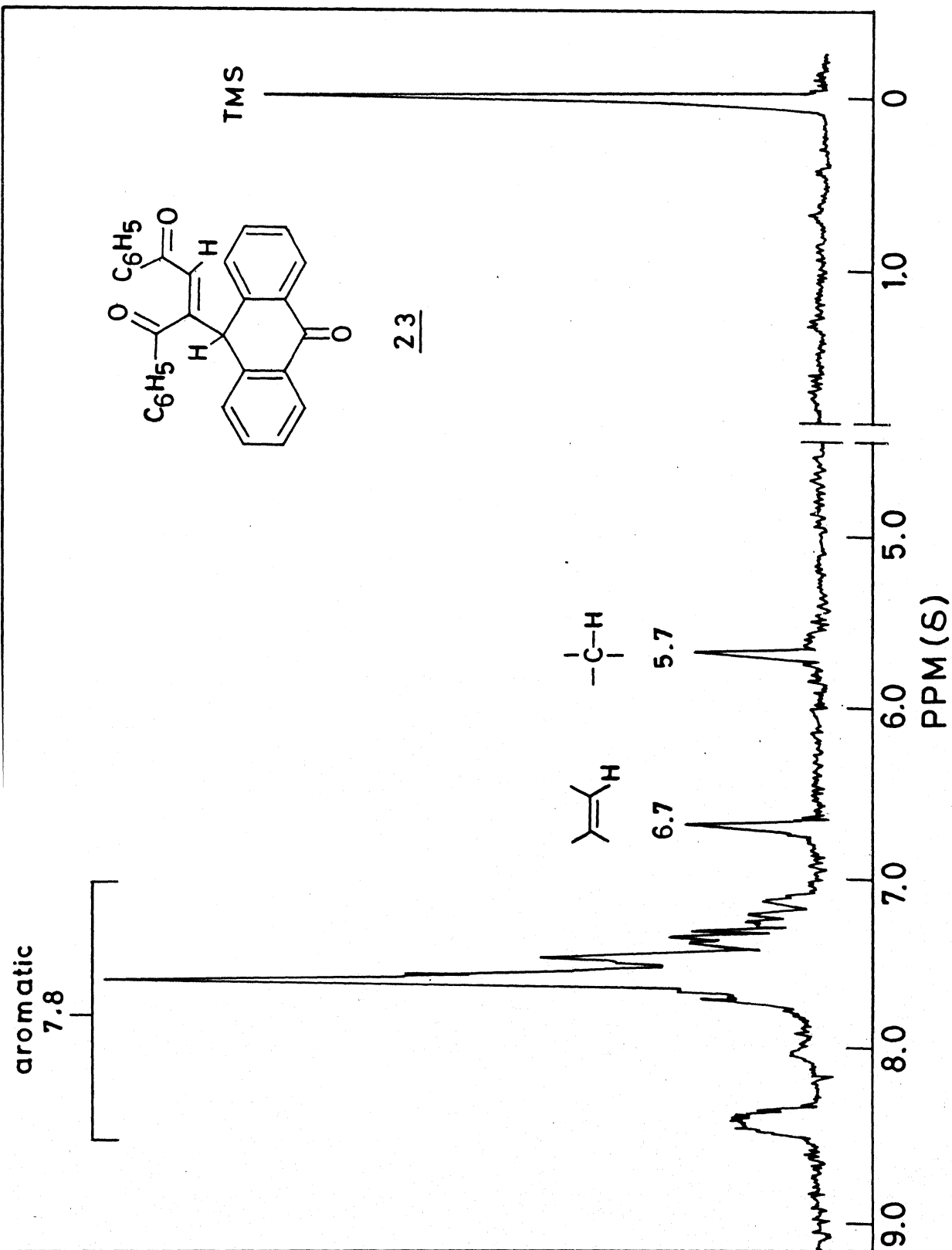
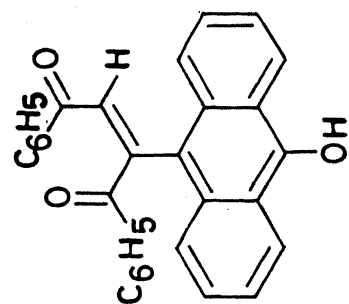


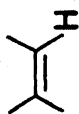
Figure II.3 ^1H NMR spectrum (90 MHz) of 23.

aromatic
7.626

TMS

O-H

3.65



6.85

0

4.0

5.0

6.0

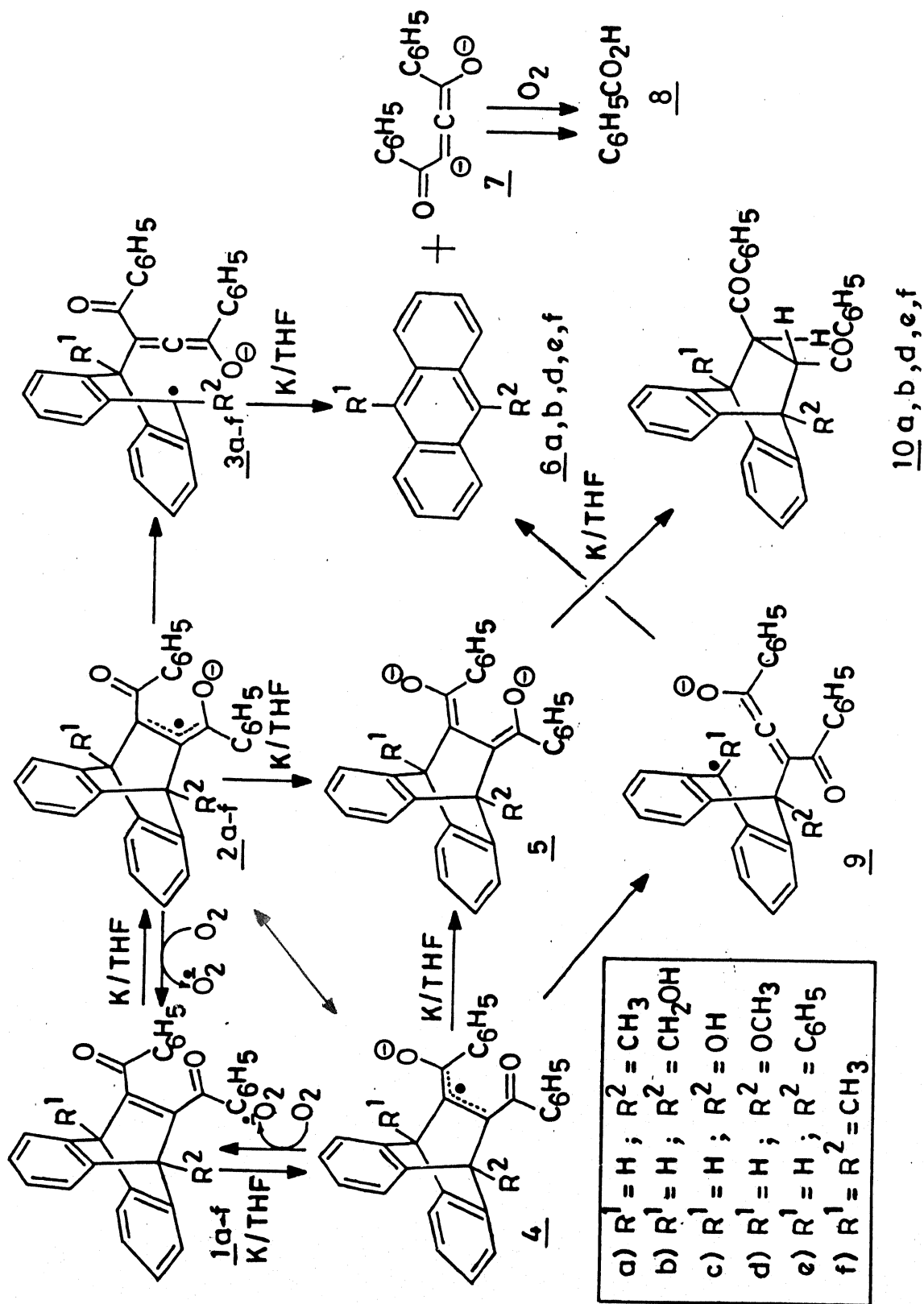
7.0

8.0

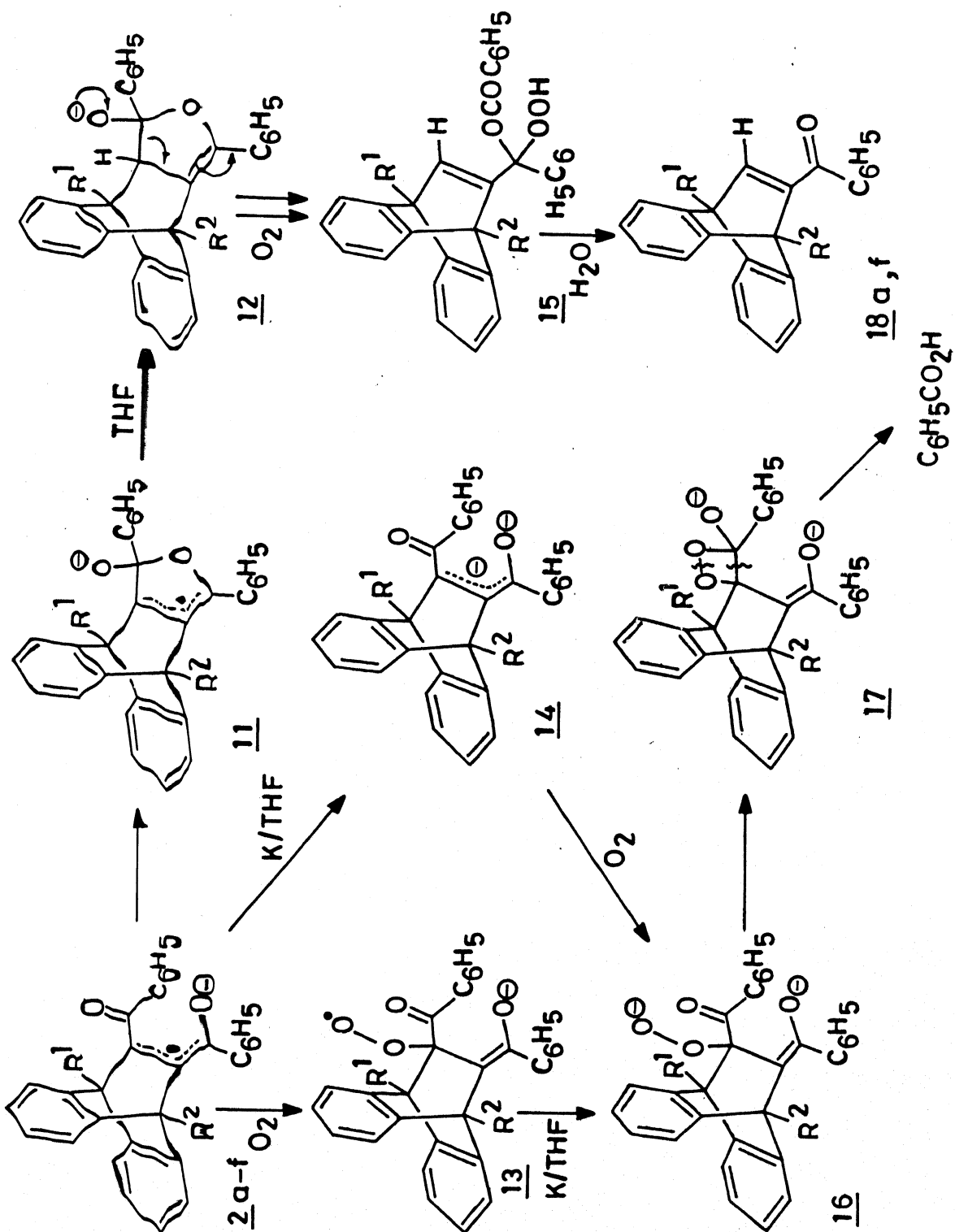
PPM (δ)Figure II.4 ^1H NMR spectrum (90 MHz) of 26.

that the ~~initial~~ step in the reaction of 1a-f with potassium involves an electron transfer process to give the corresponding radical anion intermediates 2(a-f) or 4(a-f), which in turn, can accept a second electron to give the dianion intermediates 5(a-f). These dianion intermediates 5(a-f), on workup, will give rise to the dihydrodibenzobarrelenes 10a,b,d-f (Scheme II.1). An alternative pathway for the reaction of the radical anions 2(a-f) and 4(a-f) involves a homolytic fragmentation to give the new radical anions 3(a-f) and 9(a-f), respectively, which can ultimately lead to the anthracene derivatives 6a,b,d-f and the dianion fragment 7, in each case. Further transformation of 7, under workup conditions, will lead to benzoic acid (8), one of the observed products in the reactions of 1a-f with potassium (Scheme II.1).

The formation of the monodebenzoylated products 18a,f from 1a,f could be explained in terms of the reaction pathways shown in Scheme II.2. The radical anions 2(a,f) could undergo cyclization to give the new radical anion intermediates 11(a,f), which could be subsequently converted to 12(a,f) through hydrogen atom abstraction from the solvent. Mention may be made in this connection that such cyclizations of radical anion intermediates have been observed in the reaction of o-dibenzoylbenzene with alkali metals in aprotic solvents.⁹⁻¹² Further transformation of 12(a,f) will lead to the hydroperoxy esters 15(a,f), which under the conditions of workup will lead to 18a,f and benzoic acid



Scheme II.1



Scheme II.2

8

(8) (Scheme II.2).

The formation of benzoic acid (8) in the reactions of 1a-f with potassium could also arise through other pathways, besides the transformations of the intermediate 7 (Scheme II.1) and 15 (Scheme II.2). For example, the radical anions 2(a-f) could combine with oxygen to give the corresponding hydroperoxy radical anion intermediates 13(a-f), which in turn, could lead to the dianion intermediates 16(a-f). These dianion intermediates 16(a-f) could also be formed directly from the dianion intermediates 14(a-f), through their reaction with oxygen. The dianion intermediates 16(a-f) could ultimately lead to benzoic acid (8), through the corresponding dioxetane intermediates 17(a-f), as shown in Scheme II.2.

In order to examine the possible role of oxygen in the reaction of 1a-f with potassium in THF, we have, in a separate experiment, carried out the reaction of a representative dibenzobarrelene, 1a with potassium in THF, saturated with oxygen. Under these conditions, 1a gave a mixture of 9-methylantracene (6a, 10%) and benzoic acid (8, 20%), along with a 73% recovery of the unchanged starting material (1a). The fact that 1a is recovered in large amounts under these conditions would suggest that a major pathway for the deactivation of the radical anion intermediates 2a or 4a is through a back electron transfer to oxygen, leading to the corresponding dibenzobarrelene (1a) and superoxide. The formation of small amounts of 6a and 8 in this

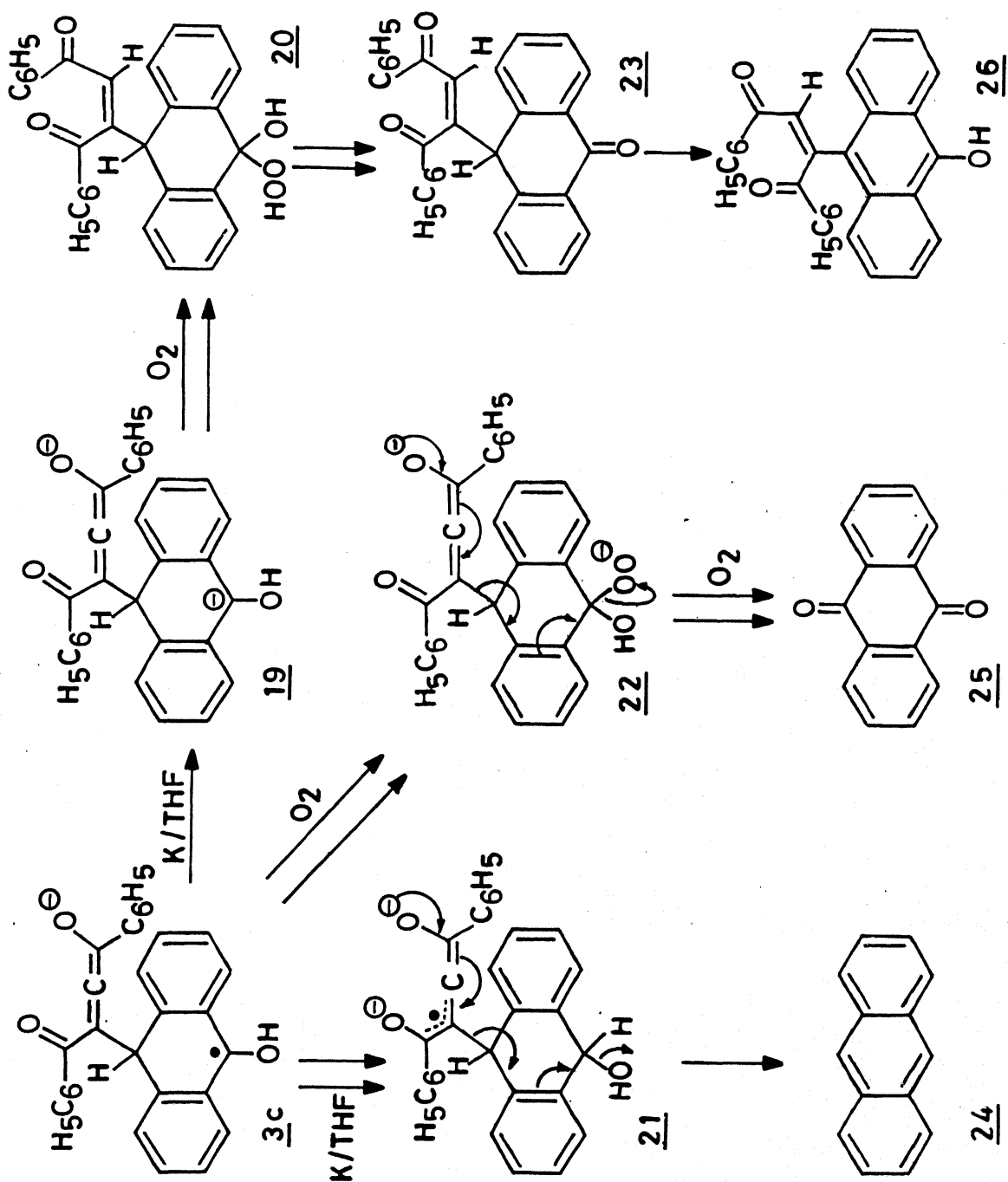
reaction, however, could be explained in terms of the reaction of 1a with superoxide or through the subsequent transformations of 2a, by pathways indicated in Schemes II.1 and II.2.

To understand the nature of the products formed in the reaction of the starting dibenzobarrelenes (1a-f) with superoxide, we have, in a separate experiment, carried out the reaction of 1a with potassium superoxide. Treatment of 1a with potassium superoxide in benzene containing 18-crown-6 gave a mixture of 9-methylanthracene (6a, 35%) and benzoic acid (8, 36%), along with a 53% recovery of the unchanged starting material (1a). The fact that similar mixtures of products, consisting of 6a and 8, are formed both in the reaction of 1a with potassium in THF, saturated with oxygen and with potassium superoxide would support our assumption that an important pathway for the formation of the observed products in the reaction of 1a with potassium in THF, saturated with oxygen is through the superoxide pathway.

It is pertinent to note that in the reaction of 1c with potassium, neither the dihydrobenzobarrelene derivative nor the debenzoylated product corresponding to 10(a,b,d-f) and 18(a,f), respectively could be observed. Instead, the product mixture consisted of small amounts of anthracene (24, 7%) anthraquinone (25, 7%) and significant amounts of the anthrone 23 (21%) and the anthrol 26 (31%), along with benzoic acid (8, 14%). The formation of these products could be understood in terms of the pathways shown in Scheme II.3. For example, the radical anion

intermediate 3c can undergo further reduction with potassium to give the dianion intermediate 19, which can subsequently react with oxygen under the conditions of workup and ultimately lead to the anthrone 23 and the anthrol 26. A second possible mode of reaction of 3c is to undergo hydrogen abstraction from the solvent, followed by reduction to give the intermediate 21, which can subsequently fragment to give anthracene (24). The formation of anthraquinone (25), on the other hand, can be explained in terms of the reaction of oxygen with the radical anion 3c to give the intermediate 22. Fragmentation of 22, followed by further oxygenation will lead to 25, as shown in Scheme II.3.

If the formation of anthraquinone (25) proceeds through the pathway shown in Scheme II.3, involving the reaction of 3c with oxygen, then one would expect higher yields of 25, when the reaction of 1c with potassium is carried out in THF, saturated with oxygen and also with potassium superoxide. Thus, the treatment of 1c with potassium in THF, saturated with oxygen gave a 6% yield of 24, 43% yield of 25, 34% yield of 26 and 37% yield of 8, whereas the reaction of 1c with potassium superoxide in benzene containing 18-crown-6 gave a 6% yield of 24, 34% yield of 25, 29% yield of 26 and 53% yield of 8. The increased yields of anthraquinone (25) in both these cases would strongly support the suggested pathway for its formation, as shown in Scheme II.3. It may be pointed out that none of the anthrone 23 could be isolated from the reaction of 1c with potassium in THF, saturated

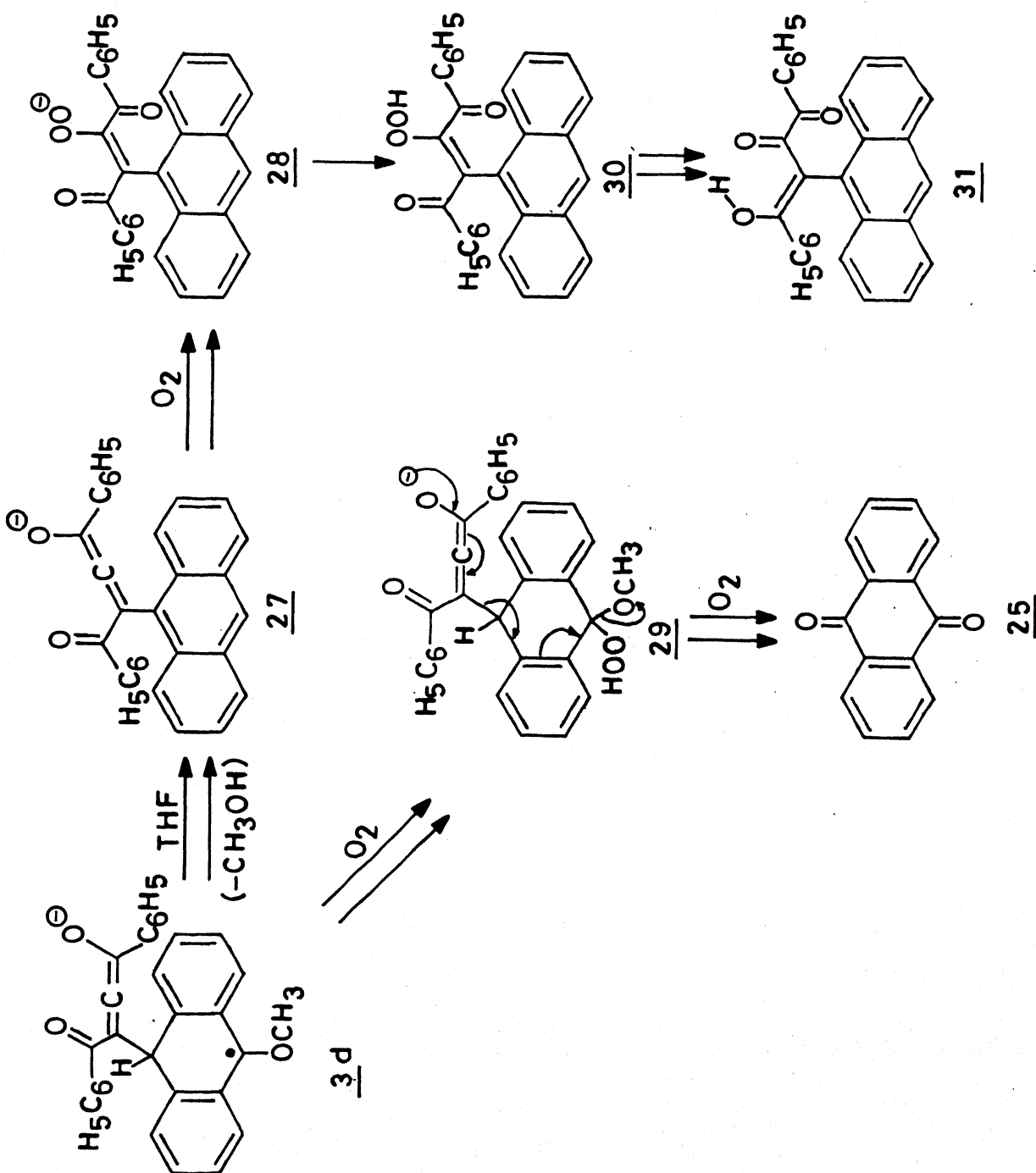


Scheme II.3

with oxygen and also with potassium superoxide. It is quite likely that the anthrone 23, formed under these conditions may get converted to the anthrol 26 by potassium superoxide, which could act as a base in bringing about this transformation.

The formation of both anthraquinone (25) and the enoldiketone 31, besides 10d, 6d, and 8 in the reaction of 1d with potassium in THF could be understood in terms of the pathways shown in Scheme II.4. Thus, the radical anion intermediate 3d, for example, through hydrogen atom abstraction, followed by loss of methanol can give the intermediate 27, which can subsequently undergo oxygenation, during workup, to give ultimately the enoldiketone 31. On the other hand, the formation of anthraquinone (25) may be proceeding through the reaction of 3d with oxygen to give the hydroperoxide intermediate 29, which can undergo fragmentation, followed by subsequent oxygenation.

To examine the role of oxygen in the reaction of 1d with potassium to give the observed products, we have carried out the reaction of 1d with potassium in THF, saturated with oxygen and also with potassium superoxide. Thus, the treatment of 1d with potassium in THF, saturated with oxygen, gave a mixture of 9-methoxyanthracene (6d, 14%), anthraquinone (25, 21%) and benzoic acid (8, 25%), along with a 61% recovery of the unchanged starting material (1d). Similarly, the reaction of 1d with potassium superoxide in benzene containing 18-crown-6 gave a mixture of



Scheme II.4

6d (14%), 25 (23%) and 8 (36%), along with a 45% recovery of the unchanged starting material (1d). The fact that none of the enoldiketone 31 and the dihydrodibenzobarrelene 10d were formed under these conditions would suggest that the radical anion 3d may be reacting with oxygen to give the oxygenated product 25 (Scheme II.4), besides undergoing fragmentation, in the usual manner (Scheme II.1), to give small amounts of 9-methoxyanthracene (6d).

II.4 CYCLIC VOLTAMMETRIC STUDIES¹⁶

In the present study, we have electrochemically generated the radical anions of the dibenzobarrelenes 1a-f. The cyclic voltammograms are shown in Figure II.5 and the reduction potentials are summarised in Table II.1. These substrates exhibited reduction potentials in the ranges -1.37 to -1.65 V and -1.91 to -2.10 V versus SSCE.

II.5 PULSE RADIOLYSIS STUDIES¹⁷

In the present investigation, the radical anions of 1a-d,f were generated in methanol and that of 1e in THF, pulse radiolytically and their absorption spectra are presented in Figure II.6. The spectral details are summarised in Table II.1. These radical anions showed absorption maxima in the regions 310-350 and 390-510 nm. It is evident from Table II.1 that these radical anions are formed from their appropriate precursors

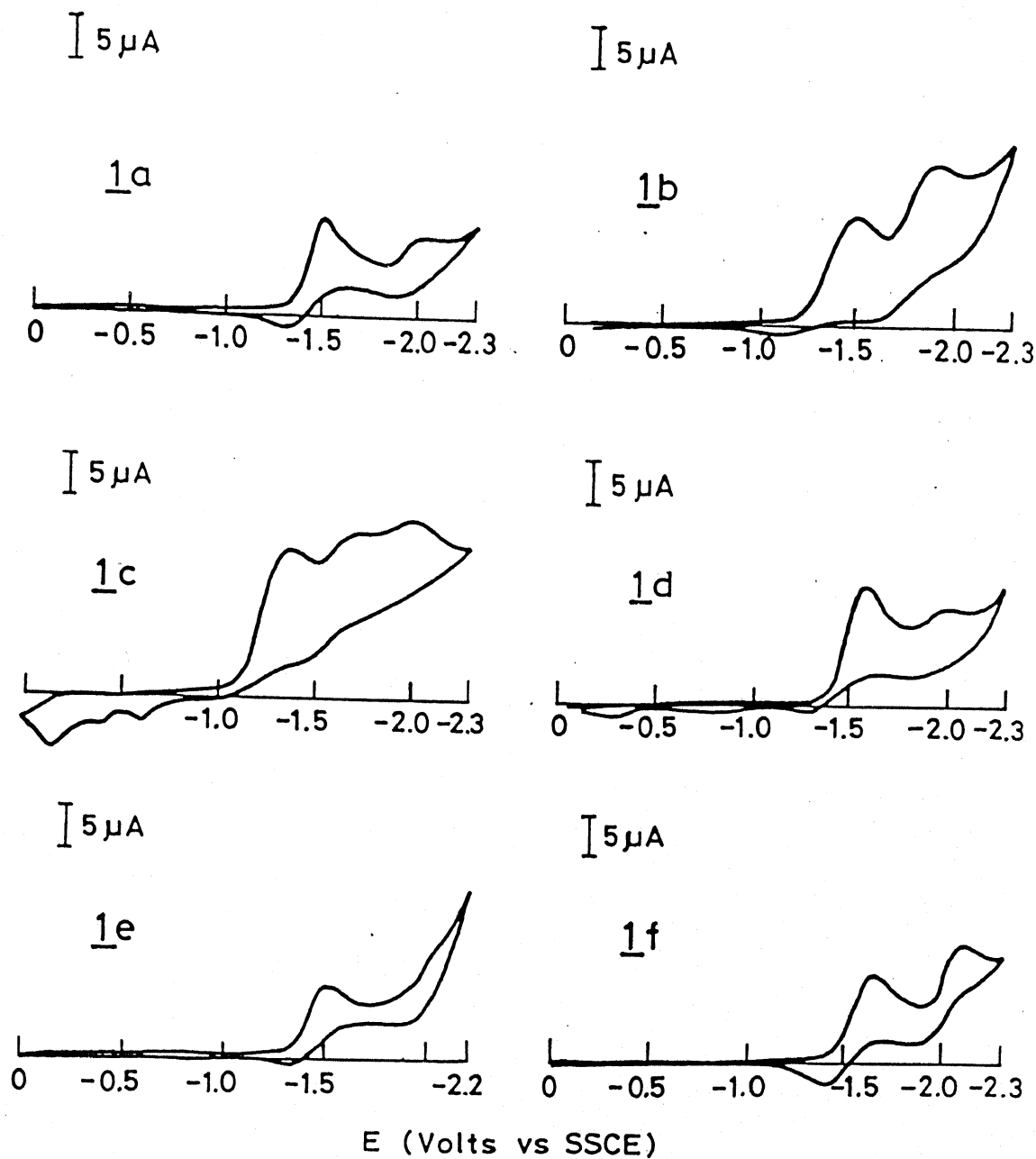


Figure II.5 Cyclic voltammograms of 1a-f

Table II.1 Electrochemical, spectral and kinetic data of dibenzobarrelenes (1a-f)

Compound	Reduction peak potential ^a E _p (V vs Ag/Ag ⁺)	Absorption maxima ^b Radical anion (nm)	k ^{b,c} (10 ¹⁰ M ⁻¹ s ⁻¹)	b,d τ _{1/2} (μs)
<u>1a</u>	-1.52, -2.02	340, 480	1.4	56
<u>1b</u>	-1.51, -1.91	350, 490	1.7	106
<u>1c</u>	-1.37, -1.70, -2.01	345, 400, 510	1.7	192
<u>1d</u>	-1.58, -2.00	355, ~ 460	1.4	76
<u>1e</u>	-1.51, -2.05	340, 490 ^e	-	1850 ^e
<u>1f</u>	-1.65, -2.10	310, 390(sh), 500	2.2	76

a, In acetonitrile containing 0.1 M tetrabutylammonium perchlorate.

b, In methanol except in the case of 1e.

c, Rate constant for the reaction between the solvated electron (e⁻_{sol}) and the substrate.

d, Half-life of the radical anion.

e, In THF.

RELATIVE ABSORBANCE CHANGE

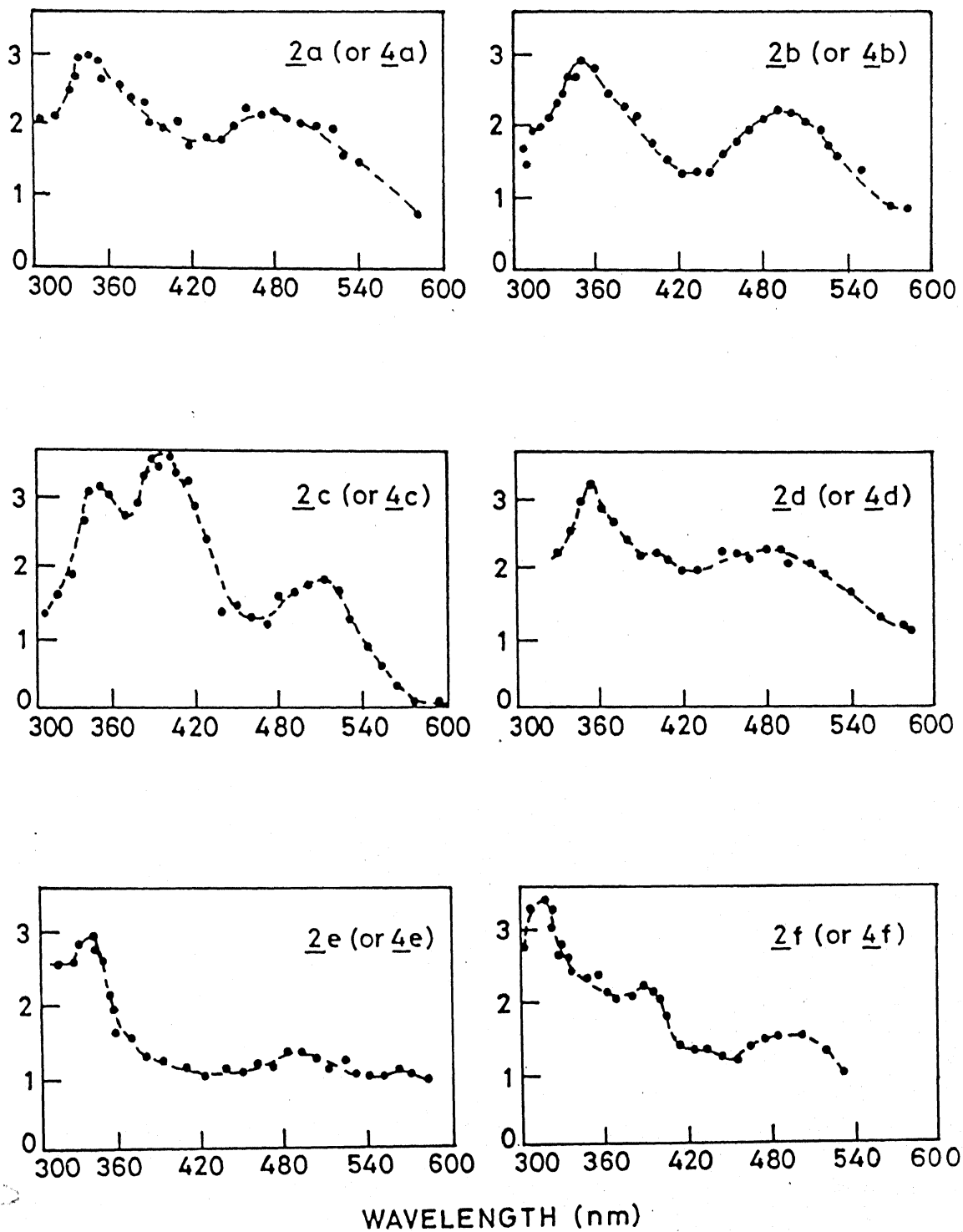


Figure II.6 Absorption spectra of the radical anions
2a-f (or 4a-f)

through the reaction with solvated electrons (e^-_{sol}) under diffusion controlled rates.

II.6 EXPERIMENTAL

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophotometers. The electronic spectra were recorded on Cary 17D, Cary 219 or Beckman DB spectrophotometers. NMR traces were recorded on Varian EM-390 or Bruker-400 MHz NMR spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-6E single focussing mass spectrometer or a Varian Mat CH7 mass spectrometer at 70 eV.

II.6.1 Starting Materials. trans-Dibenzoyl ethylene (DBE),¹⁸ mp 108-109 °C, dibenzoylacetylene (DBA),¹⁹ mp 110-111 °C, 11,12-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (1a),²⁰ mp 180-181 °C, 11,12-dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-ethenoanthracene (1b),²¹ mp 223-224 °C, 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (1c),²² mp 212-213 °C, 11,12-dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethenoanthracene (1d),²² mp 145-146 °C, 11,12-dibenzoyl-9,10-dihydro-9-phenyl-9,10-ethenoanthracene (1e),²¹ mp 263-264 °C and 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (1f),²⁰ mp 261-262 °C, were prepared by reported procedures. Petroleum ether used was the fraction with bp 60-80 °C. THF used was

dried over sodium and was distilled immediately before use. Gold Label acetonitrile was used for cyclic voltammetric studies and spectral grade methanol (Fischer Scientific) was used for pulse radiolysis.

II.6.2 Reaction of Dibenzobarrelenes (1a-f) with Potassium in THF. A general procedure was to shake a mixture of the appropriate dibenzobarrelene (1a-f) and finely cut potassium (required equivalents) in THF (125 mL) in a stoppered round bottomed flask for several hours. A few clean broken glass pieces were added to the mixture to ensure a fresh surface of metal throughout the reaction. In general, the reaction mixture underwent distinct colour changes due to the formation of the different radical anion and dianion intermediates. On completion of the reaction, the mixture was poured into moist THF (100 mL) to destroy any unchanged potassium and then the solvent was removed under vacuum to give a residual solid, which was treated with water (10 mL) and extracted with methylene chloride (100 mL). Acidification of the aqueous layer with dilute hydrochloric acid and extraction with methylene chloride (100 mL) gave the carboxylic acid fractions, which were recrystallized from suitable solvents. Workup of the non-aqueous fraction (methylene chloride extract) by removal of the solvent under vacuum and chromatographing over silica gel, followed by recrystallization from suitable solvents gave the non-acidic products.

II.6.3 Reaction of 11,12-Dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (1a) with Potassium in THF. Treatment of 960 mg (2.25 mmol) of 1a with potassium (88 mg, 2.25 mg-atom) in THF (125 mL) for 20 h and workup in the usual manner gave 125 mg (23%) of benzoic acid, mp 121 °C (mixture mp). The non-aqueous fraction (methylene chloride extract) was worked up by removal of solvent under vacuum and chromatographing over silica gel. Elution with petroleum ether gave 90 mg (21%) of 9-methylanthracene (6a), mp 80-81 °C (mixture mp). Further elution with a mixture (2:3) of benzene and petroleum ether gave 100 mg (14%) of 12-benzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (18a), mp 165-166 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3050, 2040, 2960 and 2930 (CH) and 1640 (C=O) cm^{-1} .

UV spectrum λ_{\max} (methanol): 217 nm (ϵ , 55,200), 246 (49,650), 275 (14,800) and 288 (10,350).

^1H NMR spectrum (CDCl_3): δ 2.33 (s, 3 H, methyl), 5.13 (d, $J_{10,11} = 6$ Hz, 1 H, bridgehead) and 6.8-7.6 (m, 14 H, aromatic and vinylic).

Mass spectrum, m/e (relative intensity): 322 (M^+ , 2), 236 (8), 217 ($\text{M}^+ - \text{COC}_6\text{H}_5$, 1), 202 ($\text{M}^+ - \text{CO}_6\text{H}_5$, CH_3 , 3), 192 ($\text{M}^+ - \text{C}_6\text{H}_5\text{COC}\equiv\text{CH}$, 100), 105 (31) and other peaks.

Anal. Calcd for $C_{24}H_{18}O$: C, 89.44; H, 5.59. Found: C, 89.67; H, 5.85.

Further elution of the column with a mixture (3:1) of benzene and petroleum ether gave 360 mg (37%) of 11-endo,12-exo-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethanoanthracene (10a), mp 154-155 °C (mixture mp) (lit. mp 92 °C),²³ after recrystallization from a mixture (2:3) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3060, 3040, 3020 and 2960 (CH) and 1670 (C=O) cm^{-1} .

UV spectrum λ_{\max} (methanol): 212 nm (ϵ , 33,000) and 242 (48,350).

^1H NMR spectrum (CDCl_3): δ 1.9 (s, 3 H, methyl), 4.2 (dd, $J_{10,11} = 6$ Hz, $J_{11,12} = 2$ Hz, 1 H, methine), 4.6 (d, $J_{10,11} = 6$ Hz, 1 H, bridgehead), 4.7 (d, $J_{11,12} = 2$ Hz, 1 H, methine) and 6.8-8.2 (m, 18 H, aromatic).

Anal. Calcd for $C_{31}H_{24}O_2$: C, 86.91; H, 5.6. Found: C, 87.37; H, 5.97.

In a repeat run, 1a (960 mg, 2.25 mmol) was treated with potassium (88 mg, 2.25 mg-atom) in THF, saturated with oxygen, for 20 h. Workup of the aqueous fraction as in the earlier case gave 110 mg (20%) of benzoic acid (8), mp 121 °C (mixture mp). The non-aqueous fraction gave 45 mg (10%) of 9-methylantracene (6a), mp 80-81 °C (mixture mp) (recrystallization from petroleum ether) and 700 mg (73%) of the unchanged starting material

(1a), mp 180-181 °C (mixture mp) (recrystallization from a mixture (4:1) of benzene and petroleum ether).

II.6.4 Preparation of 11-endo,12-exo-Dibenzoyl-9,10-dihydro-9-methyl-9,10-ethanoanthracene (10a). To a well stirred mixture of 9-methylanthracene (6a, 960 mg, 5 mmol) and anhydrous aluminium chloride (680 mg, 5 mmol) in methylene chloride (100 mL), maintained around 0 °C was added DBE (1.18 g, 5 mmol) in small portions, over a period of 0.25 h. The mixture was further stirred for 0.5 h and then poured into a mixture of crushed ice and dilute hydrochloric acid. The organic layer was separated and washed with aqueous sodium bicarbonate solution and dried over sodium sulphate. Removal of the solvent under reduced pressure gave a residue, which was recrystallized from a mixture (2:3) of benzene and petroleum ether to give 1.8 g (88%) of 11-endo,12-exo-dibenzoyl-9,10-dihydro-9-methyl-9,10-ethanoanthracene (10a), mp 154-155 °C.

II.6.5 Reaction of 11,12-Dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-ethenoanthracene (1b) with Potassium in THF. Treatment of 1.1 g (2.25 mmol) of 1b with 137 mg (3.5 mg-atom) of potassium in THF (125 mL) for 15 h and workup as in the earlier cases gave 130 mg (24%) of benzoic acid (8), mp 121 °C (mixture mp), from the aqueous fraction. Workup of the non-aqueous fraction gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene

and petroleum ether gave 100 mg (21%) of 9-hydroxymethylanthracene (6b), mp 163-164 °C (mixture mp). Further elution with benzene gave 200 mg (18%) of the unchanged starting material (1b), mp 223-224 °C (mixture mp).

Continued elution with a mixture (1:9) of ethyl acetate and benzene gave 350 mg (32%) of 11-endo,12-exo-dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-ethanoanthracene (10b), mp 172-173 °C.

IR spectrum ν_{\max} (KBr): 3400 (OH), 3050, 3010, 2950 and 2920 (CH) and 1670 (C=O) cm^{-1} .

UV spectrum λ_{\max} (methanol): 217 nm (ϵ , 41,250) and 245 (37,000).

^1H NMR spectrum (CDCl_3): δ 1.65 (t, 1 H, OH, D_2O exchangeable), 4.05 (dd, $J_{10,11} = 6$ Hz, $J_{11,12} = 2$ Hz, 1 H, methine), 4.55 (d, $J_{11,12} = 2$ Hz, 1 H, methine), 4.7 (d, $J = 3$ Hz, 2 H, methylene), 4.8 (d, $J_{10,11} = 6$ Hz, 1 H, bridgehead) and 7.1-8.1 (m, 18 H, aromatic).

Anal. Calcd for $\text{C}_{31}\text{H}_{24}\text{O}_3$: C, 83.78; H, 5.40. Found: C, 84.05; H, 5.76.

II.6.6 Preparation of 11-endo,12-exo-Dibenzoyl-9,10-dihydro-9-hydroxymethyl-9,10-ethanoanthracene (10b). A mixture of 9-hydroxymethylanthracene (6b, 416 mg, 2 mmol) and DBE (472 mg, 2 mmol) in toluene (50 mL) was refluxed for 36 h. The solvent was removed under vacuum and the residue, on trituration

with methanol, gave 600 mg (66%) of 10b, mp 172-173 °C, after recrystallization from a mixture (7:3) of benzene and petroleum ether.

II.6.7 Reaction of 11,12-Dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (1c) with Potassium in THF. A solution of 1c (1.93 g, 4.5 mmol) was shaken with potassium (263 mg, 6.75 mg-atom) in THF (125 mL) for 20 h and worked up in the usual manner to give 150 mg (14%) of benzoic acid (8), mp 121 °C (mixture mp), from the aqueous fraction. Workup of the non-aqueous fraction gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 60 mg (7%) of anthracene (24), mp 216 °C (mixture mp). Further elution of the column with a mixture (2:3) of benzene and petroleum ether gave 70 mg (7%) of anthraquinone (25), mp 284-285 °C (mixture mp). Subsequent elution with benzene gave 400 mg (21%) of 10-(cis-1,2-dibenzoyl-ethenyl)-9-anthrone (23), mp 173-174 °C, after recrystallization from a mixture (7:3) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3060 and 3020 (CH), 1650 and 1640 (C=O) cm^{-1} .

UV spectrum λ_{\max} (methanol): 210 nm (ϵ , 1,200) and 256 (2,450).

^1H NMR spectrum (CDCl_3): δ 5.7 (s, 1 H, methine), 6.7 (s, 1 H, vinylic) and 7.1-8.5 (m, 18 H, aromatic).

^{13}C NMR spectrum (CDCl_3): δ 47.25, 48.92, 124.68, 126.65, 127.13, 127.41, 127.50, 127.97, 128.81, 129.26, 129.52, 129.61,

130.06, 131.80, 131.94, 132.04, 132.25, 133.90, 134.04, 134.14, 134.36, 135.88, 136.38, 136.48, 139.99, 158.34, 158.44, 184.18 (C=O), 188.92 (C=O) and 197.66 (C=O).

Mass spectrum m/e (relative intensity): 428 (M^+ , 10), 410 ($M^+ - H_2O$, 6), 323 ($M^+ - C_6H_5CO$, 9), 306 ($M^+ - C_6H_5CO$, OH, 4), 193 ($M^+ - C_6H_5COCH=CCOC_6H_5$, 10), 165 ($M^+ - C_6H_5COCH=COC_6H_5$, CO, 6), 105 (100) and other peaks.

Anal. Calcd for $C_{30}H_{20}O_3$: C, 84.11; H, 4.67. Found: C, 83.78; H, 4.52.

Continued elution of the column with a mixture (1:9) of ethyl acetate and benzene gave 600 mg (31%) of 10-(cis-1,2-dibenzoyl-ethenyl)-9-anthrol (26), mp 203-204 °C (d), after recrystallization from benzene.

IR spectrum ν_{max} (KBr): 3400 (OH), 3050 and 3020 (CH), 1650 and 1640 (C=O) cm^{-1} .

UV spectrum λ_{max} (methanol): 215 nm (ϵ , 1,300) and 262 (1,100).

1H NMR spectrum ($CDCl_3$): δ 3.65 (s, 1 H, OH, D_2O exchangeable), 6.85 (s, 1 H, vinylic) and 6.91-8.3 (m, 18 H, aromatic).

^{13}C NMR spectrum ($CDCl_3$): δ 110.85, 125.24, 126.47, 126.75, 126.84, 127.20, 127.37, 127.73, 128.05, 128.22, 128.58, 128.96, 129.34, 129.60, 129.68, 129.89, 130.19, 131.07, 131.36, 131.63, 131.79, 132.13, 132.48, 132.78, 132.85, 133.33, 133.74, 134.39, 134.45, 137.74, 137.95, 139.64, 141.83, 142.01, 145.68, 147.40,

183.24 (C=O) and 189.30 (C=O).

Mass spectrum, m/e (relative intensity): 428 (M^+ , 7), 410 ($M^+ - H_2O$, 4), 323 ($M^+ - C_6H_5CO$, 5), 306 ($M^+ - C_6H_5CO, OH$, 4), 193 ($M^+ - C_6H_5COCH=CCOC_6H_5$, 4), 165 ($M^+ - C_6H_5COCH=CCOC_6H_5, CO$, 3), 105 (100) and other peaks.

Anal. Calcd for $C_{30}H_{20}O_3$: C, 84.11; H, 4.67. Found: C, 84.26; H, 4.85.

In a repeat run, 1c (856 mg, 2 mmol) was treated with potassium (117 mg, 3 mg-atom) in THF (125 mL), saturated with oxygen for 20 h. Workup of the reaction mixture as in the earlier case gave 180 mg (37%) of benzoic acid (8), mp 121 °C (mixture mp), from the aqueous fraction. The non-aqueous fraction (methylene chloride extract), after removal of the solvent, was chromatographed over silica gel. Elution with petroleum ether gave 20 mg (6%) of anthracene (24), mp 216 °C (mixture mp). Further elution with a mixture (1:1) of benzene and petroleum ether gave 180 mg (43%) of anthraquinone (25), mp 284-285 °C (mixture mp). Subsequent elution with benzene gave 290 mg (34%) of 26, mp 203-204 °C (d).

II.6.8 Conversion of 23 to 26. To a solution of 23 (50 mg, 0.12 mmol) in methanol (15 mL) was added sodium hydroxide (20 mg, 0.5 mmol) and stirred for 1 h. The reaction mixture was worked up by pouring into water and extraction with methylene chloride. Removal of the solvent under vacuum from the methylene chloride extract gave 30 mg (60%) of 26,

mp 203-204 °C (d), after recrystallization from benzene.

II.6.9 Reaction of 11,12-Dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethenoanthracene (1d) with Potassium in THF. A solution of 1d (884 mg, 2 mmol) in THF (125 mL) was shaken with potassium (78 mg, 2 mg-atom) for 15 h. Workup of the reaction mixture as in the earlier cases gave 125 mg (26%) of benzoic acid (8), mp 121 °C (mixture mp). The non-aqueous fraction, after removal of the solvent, was chromatographed over silica gel. Elution of the column with petroleum ether gave 60 mg (14%) of 9-methoxyanthracene (6d), mp 96-97 °C (mixture mp). Further elution with a mixture (3:1) of benzene and petroleum ether gave 70 mg (17%) of anthraquinone (25), mp 284-285 °C (mixture mp). Subsequent elution with benzene gave 250 mg (28%) of 11-endo, 12-exo-dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethanoanthracene (10d), mp 167-168 °C (lit. mp 161 °C),²³ after recrystallization from a mixture (7:3) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3060, 3020, 2960 and 2830 (CH) and 1670 (C=O) cm^{-1} .

UV spectrum λ_{\max} (methanol): 253 nm (ϵ , 61,250) and 275 (14,300).

¹H NMR spectrum (CDCl₃): δ 3.8 (s, 3 H, methoxy), 4.0 (dd, $J_{10,11} = 6$ Hz, $J_{11,12} = 2$ Hz, 1 H, methine), 4.5 (d, $J_{11,12} = 2$ Hz, 1 H, methine), 4.9 (d, $J_{10,11} = 6$ Hz, 1 H, bridgehead) and 6.9-8.2 (m, 18 H, aromatic).

Anal. Calcd for $C_{31}H_{24}O_3$: C, 83.78; H, 5.40. Found: C, 83.56; H, 5.18.

Continued elution with a mixture (1:9) of ethyl acetate and benzene gave 150 mg (17%) of 2-(9-anthracenyl)-1,4-diphenyl-1-hydroxybut-1-ene-3,4-dione (31), mp 189-190 °C (mixture mp),²⁴ after recrystallization from carbon tetrachloride.

In a repeat run, 1d (884 mg, 2 mmol) was treated with potassium (78 mg, 2 mg-atom) in THF (125 mL), saturated with oxygen, for 15 h. Workup as in the earlier cases gave 125 mg (25%) of benzoic acid (8), mp 121 °C (mixture mp), from the aqueous fraction. The non-aqueous fraction, after removal of the solvent, was chromatographed over silica gel. Elution with petroleum ether gave 60 mg (14%) of 9-methoxyanthracene (6d), mp 96-97 °C (mixture mp). Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 90 mg (21%) of anthraquinone (25), mp 284-285 °C (mixture mp). Subsequent elution with a mixture (4:1) of benzene and petroleum ether gave 540 mg (61%) of the unchanged starting material (1d), mp 145-146 °C (mixture mp).

II.6.10 Preparation of 11-endo,12-exo-Dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethanoanthracene (10d). A mixture of 9-methoxyanthracene (6d, 416 mg, 2 mmol) and DBE (472 mg, 2 mmol) in toluene (50 mL) was refluxed for 30 h. The solvent was removed under reduced pressure and the solid residue was triturated with methanol to give 700 mg (79%) of 10d, mp 167-168 °C, after

recrystallization from a mixture (7:3) of benzene and petroleum ether.

II.6.11 Reaction of 11,12-Dibenzoyl-9,10-dihydro-9-phenyl-9,10-ethenoanthracene (1e) with Potassium in THF. Treatment of 1.95 g (4 mmol) of 1e with 156 mg (4 mg-atom) of potassium in THF (125 mL) for 15 h and workup in the usual manner gave 300 mg (31%) of benzoic acid (8), mp 121 °C (mixture mp), from the aqueous fraction. The non-aqueous fraction, on workup gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 150 mg (15%) of 9-phenyl-anthracene (6e), mp 151-152 °C (mixture mp). Further elution with a mixture (3:2) of benzene and petroleum ether gave 1.0 g (51%) of 11-endo,12-exo-dibenzoyl-9,10-dihydro-9-phenyl-9,10-ethanoanthracene (10e), mp 197-198 °C, after recrystallization from a mixture (4:1) of benzene and petroleum ether.

IR spectrum ν_{max} (KBr): 3060 and 3020 (CH) and 1670 (C=O) cm^{-1} .

UV spectrum λ_{max} (methanol): 214 nm (ϵ , 28,650) and 242 (34,650).

^1H NMR spectrum (CDCl_3): δ 3.86 (dd, $J_{10,11} = 6$ Hz, $J_{11,12} = 2$ Hz, 1 H, methine), 4.6 (d, $J_{11,12} = 2$ Hz, 1 H, methine), 5.16 (d, $J_{10,11} = 6$ Hz, 1 H, bridgehead) and 6.5-8.0 (m, 23 H, aromatic).

Anal. Calcd for $\text{C}_{36}\text{H}_{26}\text{O}_2$: C, 88.16; H, 5.30. Found: C, 88.49; H, 5.38.

Subsequent elution with benzene gave 375 mg (19%) of the unchanged starting material (1e), mp 263-264 °C (mixture mp).

II.6.12 Preparation of 11-endo,12-exo-Dibenzoyl-9,10-dihydro-9-phenyl-9,10-ethanoanthracene (10e). DBE (472 mg, 2 mmol) was added, in small portions over a period of 0.25 h, to a well-stirred mixture of 9-phenylanthracene (6e, 508 mg, 2 mmol) and aluminium chloride (270 mg, 2 mmol) in methylene chloride (50 mL), maintained around 0 °C. The reaction mixture was stirred for an additional period of 0.5 h and poured into a mixture of crushed ice and dilute hydrochloric acid. The organic layer was washed with aqueous sodium bicarbonate solution and dried over anhydrous sodium sulphate. Removal of the solvent under vacuum and recrystallization of the residual solid from a mixture (4:1) of benzene and petroleum ether gave 750 mg (76%) of 10e, mp 197-198 °C.

II.6.13 Reaction of 11,12-Dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (1f) with Potassium in THF. Treatment of 1f (1.98 g, 4.5 mmol) with potassium (176 mg, 4.5 mg-atom) in THF (125 mL) for 15 h and workup as in the earlier cases gave 300 mg (27%) of benzoic acid (8), mp 121 °C (mixture mp), from the aqueous fraction. The non-aqueous fraction was worked up by removal of the solvent under reduced pressure and chromatographing the residual solid over silica gel. Elution with petroleum ether gave 140 mg (15%) of 9,10-dimethylanthracene (6f), mp 181-182 °C (mixture mp). Further elution with a mixture (2:3) of benzene and petroleum ether gave 450 mg (30%) of 12-benzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene

(18f), mp 131-132 °C, after recrystallization from a mixture (3:2) of benzene and petroleum ether.

IR spectrum ν_{\max} : 3050, 3030, 2960, 2930 and 2870 (CH) and 1640 (C=O) cm^{-1} .

UV spectrum λ_{\max} (methanol): 217 nm (ϵ , 46,650), 247 (42,200), 275 (8,600) and 288 (7,850).

^1H NMR spectrum (CDCl_3): δ 2.15 (s, 3 H, methyl), 2.3 (s, 3 H, methyl) and 6.9-7.6 (m, 14 H, aromatic and vinylic).

Mass spectrum, m/e (relative intensity): 336 (M^+ , 4), 321 ($\text{M}^+ - \text{CH}_3$, 1), 231 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CO}$, 100), 216 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CO}$, CH_3 , 31), 206 ($\text{M}^+ - \text{C}_6\text{H}_5\text{COC}\equiv\text{CH}$, 3), 191 ($\text{M}^+ - \text{C}_6\text{H}_5\text{COC}\equiv\text{CH}$, CH_3 , 39), 176 ($\text{M}^+ - \text{C}_6\text{H}_5\text{COC}\equiv\text{CH}$, 2 CH_3 , 1), 105 (2) and other peaks.

Anal. Calcd for $\text{C}_{25}\text{H}_{20}\text{O}$: C, 89.28; H, 5.95. Found: C, 89.10; H, 6.31.

Subsequent elution with a mixture (3:1) of benzene and petroleum ether gave 800 mg (40%) of 11-endo,12-exo-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethanoanthracene (10f), mp 184-185 °C (lit. mp 195 °C),²³ after recrystallization from a mixture (3:2) of benzene and petroleum ether.

IR spectrum ν_{\max} (KBr): 3060, 3040, 2980, 2940, 2880 (CH) and 1670 (C=O) cm^{-1} .

UV spectrum λ_{\max} (methanol): 251 nm (ϵ , 38,200).

^1H NMR spectrum (CDCl_3): δ 1.8 (s, 6 H, methyl), 4.1 (s, 2 H, methine) and 7.1-7.9 (m, 18 H, aromatic).

Anal. Calcd for $C_{32}H_{26}O_2$: C, 86.87; H, 5.88. Found: C, 87.15; H, 5.52.

II.6.14 Preparation of 11-endo,12-exo-Dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethanoanthracene (10f). To a well-stirred mixture of 9,10-dimethylantracene (6f, 412 mg, 2 mmol) and anhydrous aluminium chloride (270 mg, 2 mmol) in methylene chloride (50 mL), maintained around 0°C , DBE (472 mg, 2 mmol) was added in small portions over a period of 0.25 h and the mixture was subsequently stirred for an additional period of 1 h. Workup as in the earlier cases gave a residual solid, which after recrystallization from a mixture (3:2) of benzene and petroleum ether gave 800 mg (74%) of 10f, mp $184-185^{\circ}\text{C}$.

II.6.15 Reaction of 11,12-Dibenzoyl-9,10-dihydro-9-methyl-9,10-ethenoanthracene (1a) with Potassium Superoxide. A mixture of 1a (960 mg, 2.25 mmol), potassium superoxide (160 mg, 2.25 mmol) and 18-crown-6 (292 mg, 1.1 mmol) in benzene (100 mL) was stirred at room temperature for 15 h, protected from sunlight. The reaction mixture underwent pronounced colour changes. On completion of the reaction, the mixture was washed several times with aqueous sodium chloride solution. Removal of the solvent from the organic layer under vacuum gave a residue, which gave 150 mg (35%) of 9-methylantracene (6a), mp $80-81^{\circ}\text{C}$ (mixture mp) (recrystallization from petroleum ether) and 510 mg (53%) of the unchanged starting material (1a), mp $180-181^{\circ}\text{C}$ (mixture mp) (recrystallization from a mixture (4:1) of benzene

and petroleum ether).

The combined aqueous fractions was acidified with dilute hydrochloric acid and extracted with benzene. Removal of the solvent from the benzene extract under reduced pressure gave 200 mg (36%) of benzoic acid (8), mp 121 °C (mixture mp).

II.6.16 Reaction of 11,12-Dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (1c) with Potassium Superoxide.
A mixture of 1c (856 mg, 2 mmol), potassium superoxide (142 mg, 2 mmol) and 18-crown-6 (265 mg, 1 mmol) in benzene (100 mL) was stirred at room temperature for 20 h. The reaction mixture was worked up as in the earlier case to give both aqueous and non-aqueous fractions. Workup of the non-aqueous fraction by removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 20 mg (6%) of anthracene (24), mp 216 °C (mixture mp). Further elution with a mixture (2:3) of benzene and petroleum ether gave 140 mg (34%) of anthraquinone (25), mp 284-285 °C (mixture mp). Subsequent elution with benzene gave 250 mg (29%) of 10-(cis-1,2-dibenzoyl-ethenyl)-9-anthrol (26), mp 203-204 °C (d). Workup of the aqueous fraction as in the earlier cases gave 260 mg (53%) of benzoic acid (8), mp 121 °C (mixture mp).

II.6.17 Reaction of 11,12-Dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethenoanthracene (1d) with Potassium Superoxide.
A mixture of 1d (884 mg, 2 mmol), potassium superoxide (142 mg,

2 mmol) and 18-crown-6 (265 mg, 1 mmol) in benzene (100 mL) was stirred at room temperature for 15 h and worked up to give both aqueous and non-aqueous fractions. The organic layer was worked up by removal of the solvent under reduced pressure and chromatographing the residual solid over silica gel. Elution with petroleum ether gave 60 mg (14%) of 9-methoxyanthracene (6d), mp 96-97 °C (mixture mp). Further elution with a mixture (1:1) of benzene and petroleum ether gave 95 mg (23%) of anthraquinone (25), mp 284-285 °C (mixture mp). Subsequent elution of the column with a mixture (3:1) of benzene and petroleum ether gave 400 mg (45%) of the unchanged starting material (1d), mp 145-146 °C (mixture mp). Workup of the aqueous fraction, as in the earlier cases, gave 175 mg (36%) of benzoic acid (8), mp 121 °C (mixture mp).

II.6.18 Cyclic Voltammetry. Measurements were made with a Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat, a PAR Model 175 Universal Programmer and a Kipp and Zonen X-Y recorder. Experiments were performed in a standard three compartment cell equipped with a Pt-disc working electrode, a Pt-wire counter electrode and a saturated sodium chloride-calomel electrode (SSCE). Cyclic voltammograms were recorded in deaerated acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP).

II.6.19 Pulse Radiolysis. The pulse radiolysis experiments were carried out using a computer controlled apparatus²⁵

and the irradiations were carried out with 5 ns electron pulses from the Notre Dame 8 MeV ARCO LP-7 linear accelerator, using dose rates of $\sim 2 \times 10^{16}$ eV/g per pulse. The solutions (0.2-0.5 mM) of the substrates were taken in graduated 250 mL cylindrical reservoirs and deaerated by bubbling nitrogen for at least 0.5 h prior to irradiation. Nitrogen bubbling was continued in the reservoir from which the solution was allowed to flow continuously through the cell (1 cm pathlength). The rate constants for the reactions with solvated electrons (e_{sol}^-) were determined from the kinetic analysis of the enhanced rate of decay of e_{sol}^- in the presence of the substrate or from the growth rate of the radical anion.

II.7 REFERENCES

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CHAPTER III

ELECTRON TRANSFER REACTIONS. REACTION OF EPOXYKETONES AND BENZOYLAZIRIDINES WITH POTASSIUM

III.1 ABSTRACT

The reaction of a few 1,2- and 1,4-epoxyketones (1a,b, 34a,b) and benzoylaziridines (46a-d) with potassium in tetrahydrofuran (THF) has been investigated. It has been suggested that the radical anions generated from these substrates through electron transfer processes, are the primary intermediates involved, which undergo subsequent transformations to give the observed products. Thus, the reaction of the chalcone epoxides 1a,b with potassium in THF, for example, gave a mixture of acetophenone (13), the corresponding chalcones 4a,b, dihydrochalcones 20a,b, cyclopentene isomers 21a,b and 22a,b, hydroxyacids 15a,b and benzoic acid (12a). In the case of 1b, however, besides the above mentioned products, *p*-toluic acid (12b) was also obtained. On the other hand, the reaction of a 1,4-epoxyketone such as 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (34a) with potassium gave the deoxygenated product, *o*-dibenzoylbenzene (38a) and benzoic acid (12a), besides a small amount of the unchanged starting material (34a). However, when 2,3-dibenzoyl-1,4-dihydro-1,4-diphenyl-1,4-epoxynaphthalene (34b) was treated with potassium, a mixture of products consisting

of 1,3-diphenylisobenzofuran (40b), 2-benzoyl-1,4-diphenyl-naphthalene (45b), 2,3-dibenzoyl-1,4-diphenylnaphthalene (38b), o-dibenzoylbenzene (38a) and benzoic acid (12a) was obtained.

In continuation of our studies, we have examined the reactions of some aziridine derivatives such as 46a-d and 61 with potassium in THF. Treatment of the benzoylaziridines 46a-d with potassium in THF, for example, gave the stilbenes 57a,c, hydroxyamides 51a,c,d and carboxylic acids 12a,b. The reaction of 1-cyclohexyl-6-(cyclohexylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-b]azirine (61), on the other hand, gave a mixture of 1-phenyl-4-cyclohexylaminoisoquinoline (64) and 2-cyclohexyl-3-hydroxy-3-phenylphthalimidine (68). Cyclic voltammetric and pulse radiolysis studies have been carried out, in an attempt to characterize the radical anion and dianion intermediates involved in these reactions. Reasonable mechanisms have been proposed to account for the formation of the different products in these transformations.

III.2 INTRODUCTION

Several reactions of epoxy compounds with alkali metals are reported in the literature.¹⁻⁹ In general, it has been observed that alkali metals react with epoxy compounds in aprotic solvents to give a variety of products, depending on the nature of the starting epoxide and the alkali metal used. Thus, in the reaction of epoxy compounds with lithium, for

example, deoxygenation, leading to olefins is the predominant reaction, whereas the reaction of epoxy compounds with sodium is reported to give a mixture of carbonyl compounds, alcohols and dimeric products.⁸ In contrast to the reaction of epoxy compounds, only very few examples of the reaction of aziridines with alkali metals are reported in the literature. The reaction of 1,2,3-triphenylaziridine with sodium in liquid ammonia, for example, has been shown to give 1-anilino-1,2-diphenylethane, whereas the reaction of 2,2-diphenyl-3-methylaziridine, under analogous conditions, gave diphenylmethane as the only product.⁶

There has been so far, no report in the literature on the reaction of epoxyketones and benzoylaziridines with alkali metals such as potassium in polar aprotic solvents such as THF. In this context, it was felt worthwhile to investigate the reactions of some representative epoxyketones and benzoyl aziridines with potassium in THF, to examine the type of products formed in these cases and also their reaction pathways.

III.3 RESULTS AND DISCUSSION

The epoxyketones and benzoylaziridines that we have examined in the present study include, trans-1,3-diphenyl-2,3-epoxypropan-1-one (1a), trans-2,3-epoxy-1-phenyl-3-p-tolylpropan-1-one (1b), 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (34a), 2,3-dibenzoyl-1,4-dihydro-1,4-diphenyl-1,4-epoxynaphthalene (34b), trans-2-benzoyl-1-cyclohexyl-3-phenylaziridine

(46a), cis-2-benzoyl-1-cyclohexyl-3-phenylaziridine (46b), cis-2-benzoyl-1-cyclohexyl-3-p-tolylaziridine (46c) and cis-1-cyclohexyl-2-phenyl-3-p-tolylaziridine (46d). In addition, the reaction of 1-cyclohexyl-6-(cyclohexylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-b]azirine (61) with potassium in THF has also been studied.

The reaction of 1a with potassium in THF, for example, gave a mixture of acetophenone (13, 5%), benzalacetophenone (4a, 4%), 1,3-diphenylpropan-1-one (20a, 5%), 5-benzoyl-1,3,4-triphenylcyclopent-1-ene (21a, 11%), 1-benzoyl-2,4,5-triphenylcyclopent-1-ene (22a, 3%), 2,3-diphenyl-2-hydroxypropanoic acid (15a, 26%) and benzoic acid (12a, 33%). Similarly, the reaction of 1b with potassium in THF gave a mixture of acetophenone (13, 3%), 4-methylbenzalacetophenone (4b, 3%), 1-phenyl-3-p-tolylpropan-1-one (20b, 4%), 5-benzoyl-3,4-di-p-tolyl-1-phenylcyclopent-1-ene (21b, 4%), 1-benzoyl-4,5-di-p-tolyl-2-phenylcyclopent-1-ene (22b, 11%), 2-hydroxy-2-phenyl-3-p-tolylpropanoic acid (15b, 29%), benzoic acid (12a, 31%) and p-toluic acid (12b, 7%). The reaction of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (34a) with potassium in THF, under analogous conditions, on the other hand, gave a mixture of o-dibenzoylbenzene (38a, 70%) and benzoic acid (12a, 15%), along with a 5% recovery of the unchanged starting material (34a). The reaction of 2,3-dibenzoyl-1,4-dihydro-1,4-diphenyl-1,4-epoxynaphthalene (34b) with potassium in THF, likewise, gave a mixture of products, consisting of 1,3-diphenyl-

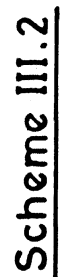
isobenzofuran (40b, 41%), 2-benzoyl-1,4-diphenylnaphthalene (45b, 13%), 2,3-dibenzoyl-1,4-diphenylnaphthalene (38b, 21%), o-dibenzoylbenzene (38a, 13%) and benzoic acid (12a, 41%). The structures of all these products were established on the basis of analytical data, spectral evidence and comparison with authentic samples, wherever possible.

The formation of the different products in the reaction of 1a,b and 34a,b with potassium can be understood in terms of the pathways shown in Schemes III.1-III.4. The initial step in the reaction of 1a,b with potassium, for example, could be the formation of the corresponding radical anions 2(a,b), which, on hydrogen atom abstraction from the solvent will give the hydroxy intermediates 3(a,b) and ultimately the deoxygenated products 4a,b. The formation of benzoic acid (12a) in these reactions could be explained in terms of the reaction of the hydroxy intermediates 3(a,b) with oxygen to give the peroxy anion intermediate 9, which can subsequently give rise to the dioxetane intermediate 14. Further fragmentation of 14 will lead to benzoic acid (12a), as shown in Scheme III.1.

A second possible mode of reaction of the starting epoxyketones 1a,b is through their conversion to the dianion intermediates 6(a,b), by a two electron reduction pathway. These dianion intermediates 6(a,b) can subsequently fragment to the corresponding aldehydes 7a,b and a new dianion intermediate 8. Further transformation of 8, under workup conditions will lead

to acetophenone (13), whereas, the aldehydes 7a,b will lead ultimately to the corresponding carboxylic acids 12a,b. Yet another mode of transformation of 1a,b will be through the dianion intermediates 5(a,b) which can subsequently rearrange to 11(a,b) via 10(a,b). Further transformations of 11(a,b) under workup conditions will lead to the hydroxycarboxylic acids 15a,b, as shown in Scheme III.1.

The formation of the dihydrochalcones 20a,b and the cyclopentene isomers 21a,b and 22a,b from 1a,b may be rationalized in terms of the further reactions of the initially formed chalcones 4a,b, as shown in Scheme III.2. It is assumed that the chalcones 4a,b accept an electron from potassium to give the corresponding radical anion intermediates 16(a,b), which can, on further reduction, lead to the corresponding dianion intermediates 17(a,b) and ultimately, the dihydrochalcones 20a,b. Alternatively, the radical anion intermediates 16(a,b) can undergo dimerization to give the dianion intermediates 19(a,b), which can subsequently lead to the cyclopentene derivatives 21a,b and 22a,b, as shown in Scheme III.2. A second pathway for the formation of the dimeric dianion intermediates 19(a,b), will be through the reaction of 17(a,b) with the initially formed chalcones 4a,b. It may be pointed out, in this connection, that the formation of similar cyclopentene derivatives has been reported earlier in the polarographic reduction of chalcones.¹⁰ Thus, the polarographic reduction of 4a in the



Scheme III.2

presence of carbon dioxide, for example, was found to give a monomeric dicarboxylic acid and a dimeric monocarboxylic acid. The latter, on decomposition, gave 1,3,4-triphenyl-1-hydroxy-2-benzoylcyclopentane. Mention may also be made of the reported reaction of a chalcone dimer, 1,3,4,6-tetraphenylhexane-1,6-dione with sodium to give 1-benzoyl-2,4,5-triphenylcyclopent-1-ene.¹¹

With a view to ascertaining whether benzalacetophenone (4a) could be an intermediate in the overall transformation of 1a to 22a, we have examined the reaction of 4a with potassium in THF, in a separate experiment. Treatment of 4a with potassium in THF gave a mixture of products consisting of 1,3-diphenylpropan-1-one (20a, 30%), 1-benzoyl-2,4,5-triphenylcyclopent-1-ene (22a, 4%) and benzoic acid (12a, 20%). The formation of 22a, under these conditions will support our assumption that it arises through the subsequent reactions of the initially formed 4a.

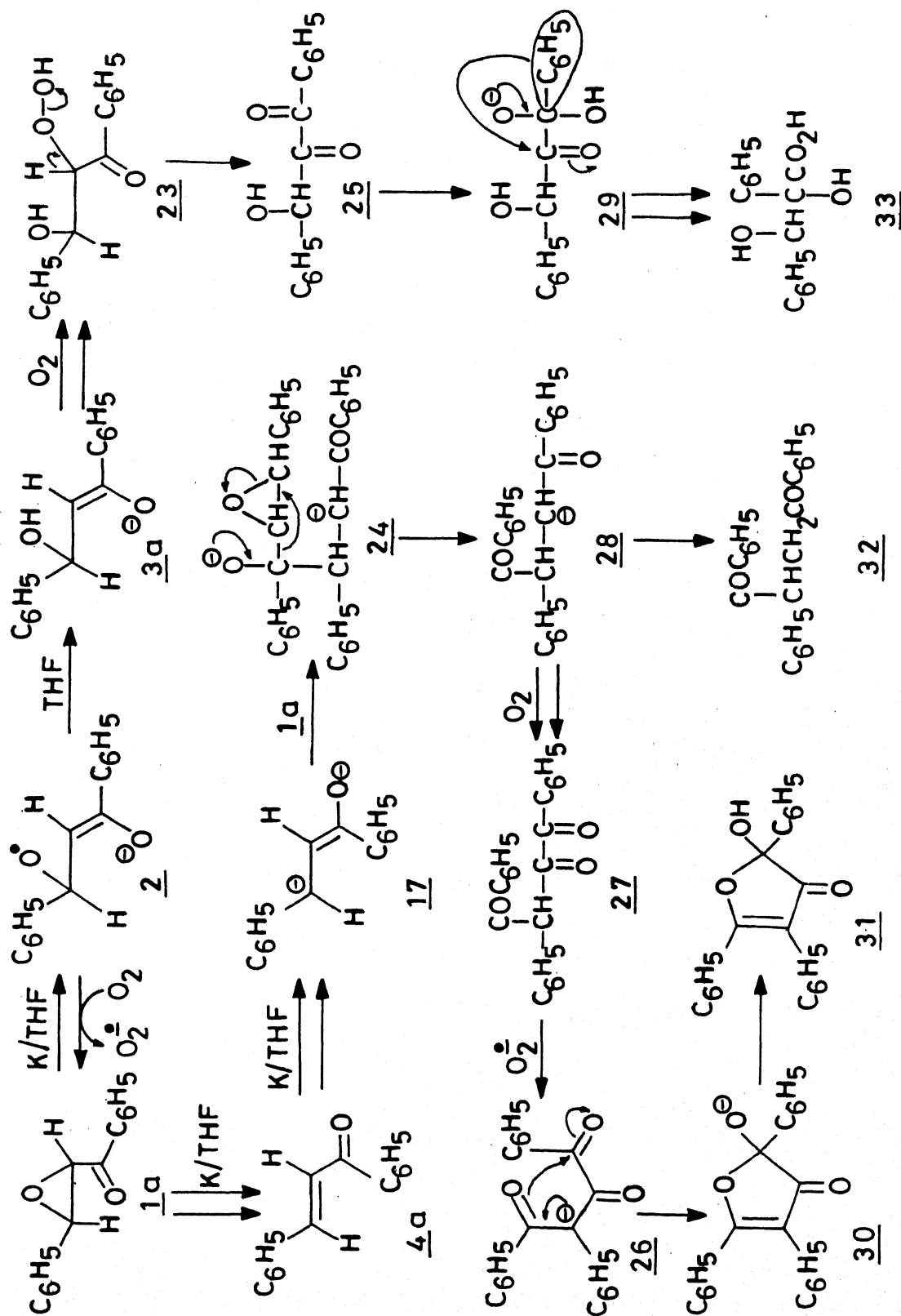
In order to examine the role of oxygen, if any, in the reaction of 1a,b with potassium, we have carried out in a separate experiment, the reaction of 1a with potassium in THF, saturated with oxygen. The reaction of 1a, under these conditions gave a mixture of benzalacetophenone (4a, 3%), 1,3-diphenylpropan-1-one (20a, 10%), 1,2,4-triphenylbutan-1,4-dione (32, 19%), 2-hydroxy-2,4,5-triphenyl-3(2H)-furanone (31, 8%), 2,3-dihydroxy-2,3-diphenylpropanoic acid (33, 4%) and benzoic acid

(12a, 25%), along with a 18% recovery of the unchanged starting material (1a).

The formation of the different products in the reaction of 1a with potassium in oxygen-saturated THF can be understood in terms of the pathways shown in Scheme III.3. The hydroxy anion intermediate 3a formed from 1a can give rise to the hydroperoxy intermediate 23, on reaction with oxygen. The loss of elements of water from 23 will give the hydroxy diketone 25, which can subsequently undergo rearrangement to give the hydroxy carboxylic acid 33.

The formation of 1,2,4-triphenylbutan-1,4-dione (32) in the reaction of 1a with potassium in oxygen-saturated THF can be understood in terms of the pathways shown in Scheme III.3, involving benzalacetophenone (4a), as intermediate. The dianion 17, generated from 4a can react with the starting epoxyketone 1a to give the intermediate 24, which can subsequently fragment to the anionic species 28. Protonation of 28, under the workup conditions will give 32. The anionic intermediate 28 can also lead to the triketone 27, through its reaction with oxygen. Further transformations of 27, as shown in Scheme III.3 will lead to the hydroxyfuranone 31.

To examine whether some of the oxygenated products formed in the reaction of 1a with potassium in THF, saturated with oxygen arise through the involvement of superoxide, we have



Scheme III.3

examined the reaction of 1a with potassium superoxide, in a separate experiment. Thus, the treatment of 1a with potassium superoxide in benzene containing 18-crown-6 gave a mixture of 31 (16%), 33 (12%) and 12a (37%), along with a 18% recovery of the unchanged starting material (1a). The fact that both 31 and 33 are observed in the reaction of 1a with potassium in THF, saturated with oxygen and also with potassium superoxide would indirectly support some of the pathways outlined in Scheme III.3.

The formation of the different products in the reaction of 1,4-epoxyketones 34a,b can be rationalized in terms of the pathways shown in Scheme III.4. The radical anion intermediate 35a, formed in the reaction of 34a with potassium, for example, can fragment to give a new radical anion intermediate 36, which can ultimately lead to benzoic acid (12a), whereas the dianion intermediate 37a, formed through a two electron reduction of 34a, could be the precursor of *o*-dibenzoylbenzene (38a). Likewise in the reaction of 34b with potassium, both benzoic acid (12a) and 1,3-diphenylisobenzofuran (40b) could arise through the intermediate 36b, whereas, the deoxygenated products 38b and 45b could arise from the dianion intermediate 37b, as shown in Scheme III.4.

With a view to ascertaining whether any oxygen is involved in the overall transformations of 34a,b to the different observed products, we have examined the reaction of 34a,b with potassium in THF, saturated with oxygen. Thus, the treatment



Scheme III.4

to oxygen, leading to the formation of superoxide. This superoxide, in turn, may be reacting with 34a,b to give the observed products.

In continuation of our studies, we have examined the reactions of a few aziridine derivatives such as 46a-d and 61 with potassium in THF. Treatment of 46a with potassium in THF gave a mixture of trans-stilbene (57a, 31%), N-cyclohexyl-2,3-diphenyl-2-hydroxypropanamide (51a, 37%) and benzoic acid (12a, 37%). Similarly, the reaction of 46b with potassium in THF gave a mixture of 57a (33%), 51a (34%) and 12a (39%). The reaction of 46c, under analogous conditions, gave a mixture of trans-1,2-di-p-tolyethylene (57c, 29%), N-cyclohexyl-2-hydroxy-2-phenyl-3-p-tolylpropanamide (51c, 33%) and benzoic acid (12a, 39%), whereas cis-1-cyclohexyl-2-phenyl-3-p-tolylaziridine (46d) gave a mixture of trans-stilbene (57a, 36%), N-cyclohexyl-2-hydroxy-3-phenyl-2-p-tolylpropanamide (51d, 42%) and p-toluic acid (12b, 38%). In contrast to the reactions of 46a-d, the reaction of 1-cyclohexyl-6-(cyclohexylimino)-1,1a,6,6a-tetrahydro-1a-phenyl-indeno[1,2-b]azirine (61) with potassium in THF gave a mixture of 1-phenyl-4-cyclohexylaminoisoquinoline (64, 64%) and 2-cyclohexyl-3-hydroxy-3-phenylphthalimidine (68, 13%). The structures of all these products were established on the basis of analytical results, spectral data and comparison with authentic samples, wherever possible.

The structure of 51a was confirmed through its independent synthesis, through reported procedures. The structures of 51c and 51d were assigned basing on their spectral analogies with 51a. The ^1H NMR spectrum of a representative example 51a (Figure III.1), for example, showed a multiplet at δ 1.3 (10 H) assigned to cyclohexyl methylene protons. The singlet at δ 2.55 (1 H, D_2O exchangeable) was assigned to the hydroxyl proton. The doublets at δ 3.0 ($J = 14$ Hz, 1 H) and δ 3.85 ($J = 14$ Hz, 1 H) were assigned to the methylene protons (inequivalent due to the adjacent asymmetric center). The multiplet at δ 3.6 (1 H) was assigned to the cyclohexyl methine proton and the broad peak at δ 6.45 (1 H) was assigned to the amide proton, whereas the aromatic protons appeared as a complex multiplet centred at δ 7.36 (10 H).

The formation of the different products in the reaction of 46a-d with potassium can be explained in terms of the pathways shown in Scheme III.5. The dianion intermediates 47(a, c, d) formed from 46a-d, for example, can lead to the hydroperoxy intermediates 52(a, c, d) through the intermediates 48(a, c, d) and 49(a, c, d), as shown in Scheme III.5. Loss of elements of water from 52(a, c, d) will lead to the observed products 51a, c, d. The starting benzoylaziridines 46a-d could also undergo a different mode of cleavage, on treatment with potassium, to give the radical anion intermediates 50 which can undergo subsequent cleavage,

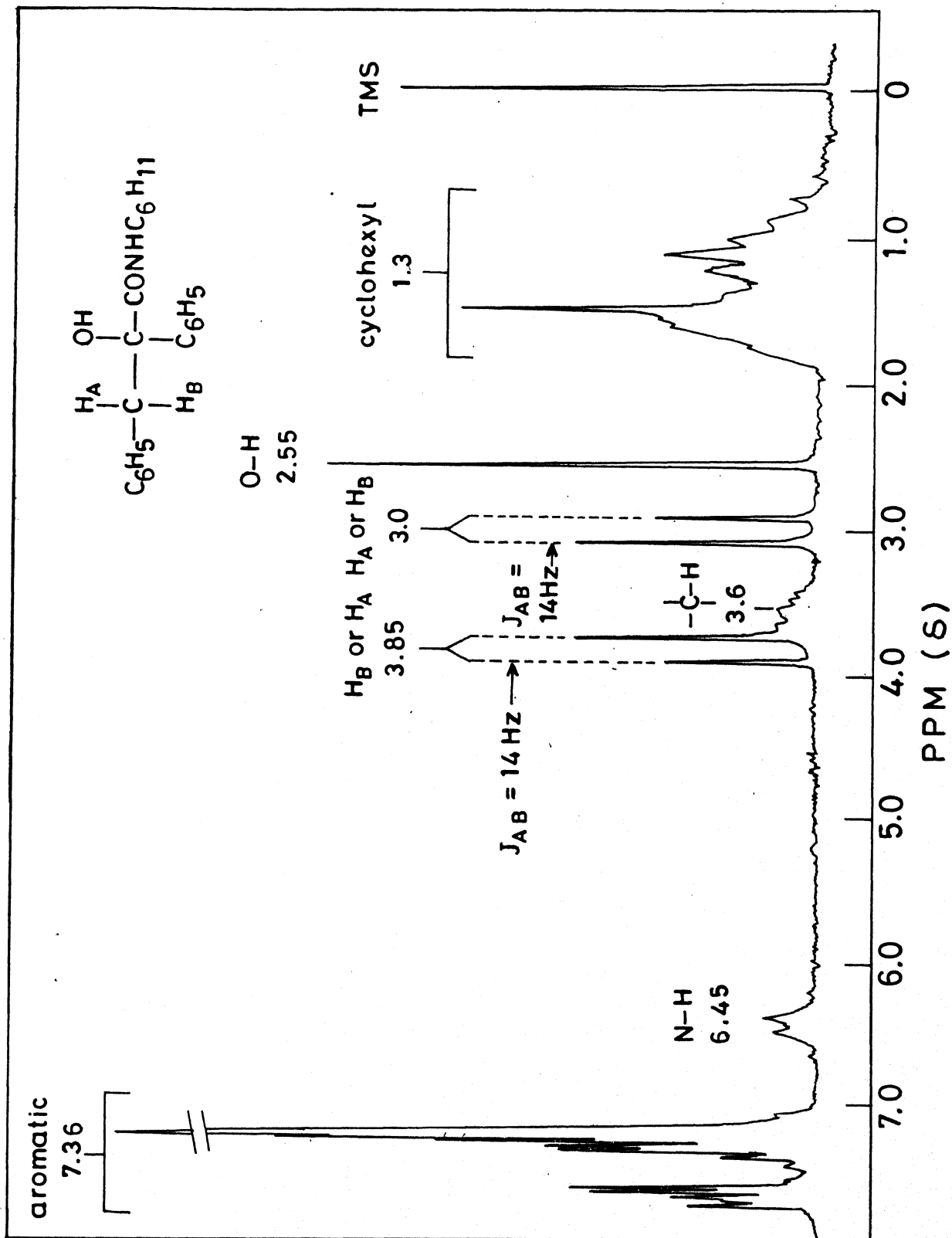
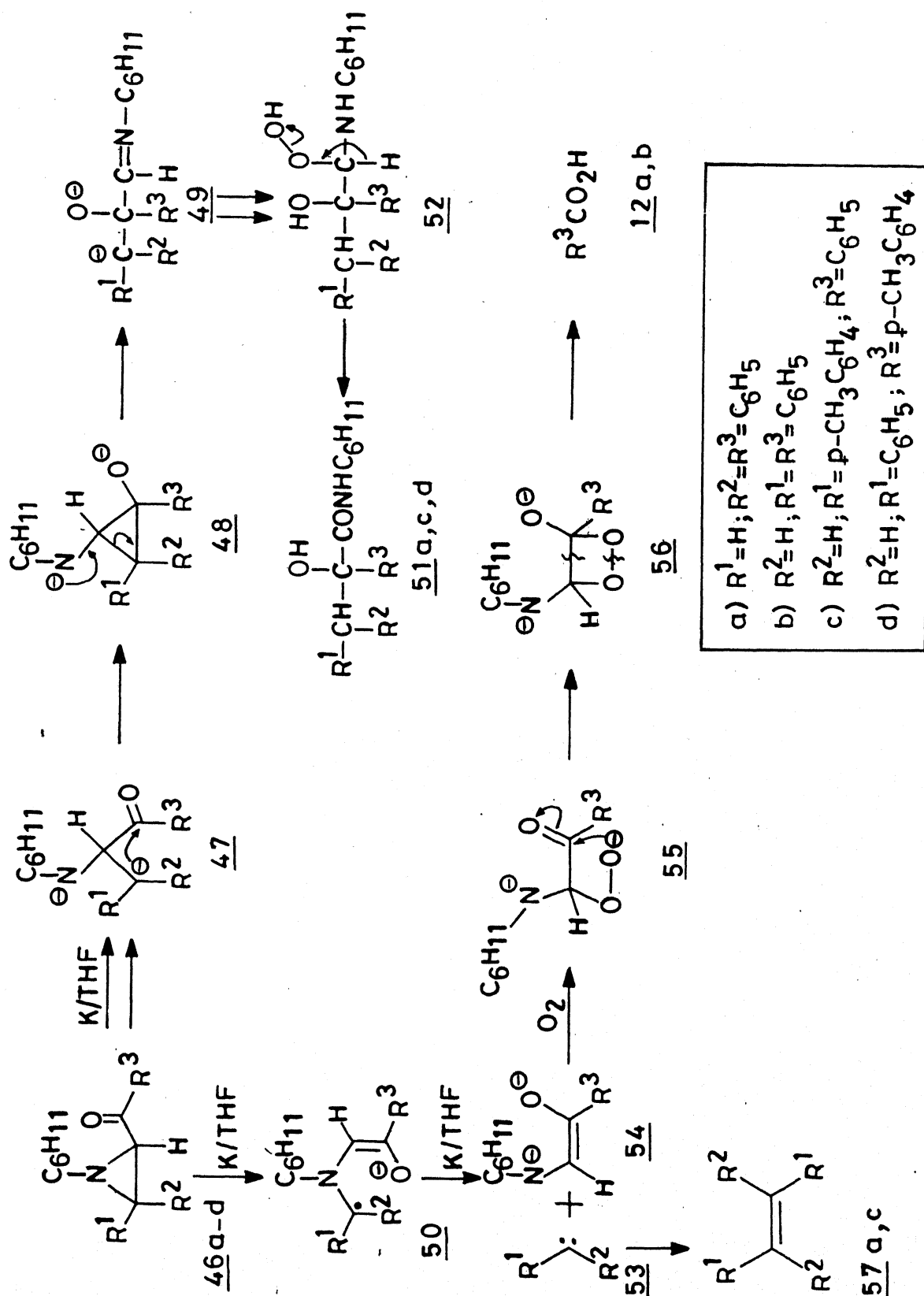


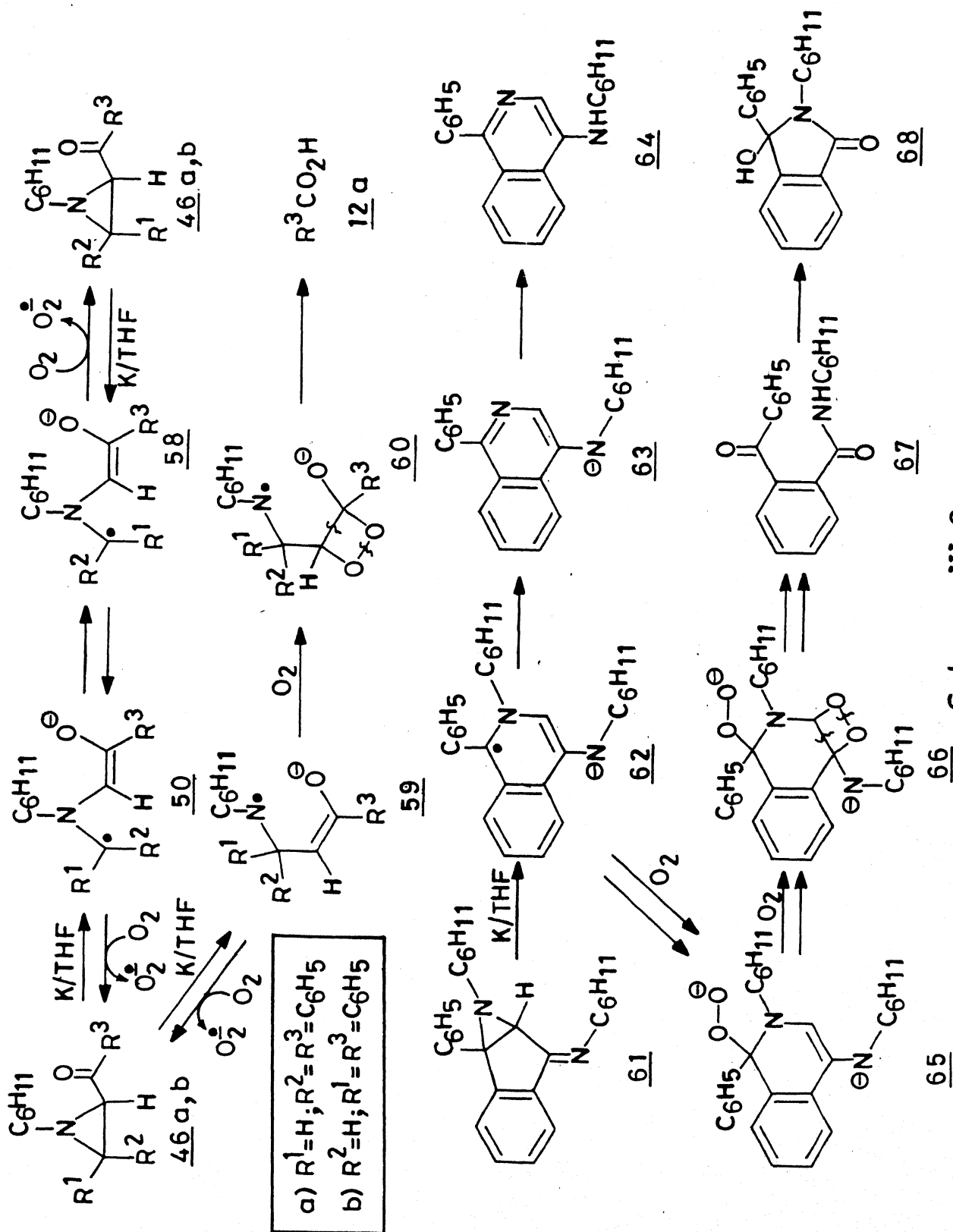
Figure III.1 ¹H NMR spectrum (80 MHz) of 51a.



Scheme III.5

on further reaction with potassium to give the carbene intermediates 53(a,c) and the dianion intermediate 54. Dimerization of the carbene intermediates 53(a,c) will lead to the stilbenes 57a,c, whereas the reaction of 54 with oxygen, will ultimately lead to the carboxylic acids 12a,b, through the intermediates 55 and 56, as shown in Scheme III.5.

In separate experiments, we have carried out the reactions of 46a,b with potassium in THF, saturated with oxygen, to ascertain the role of oxygen, if any, in the formation of the different products. Thus, the reaction of 46a, under these conditions, gave a mixture of trans-stilbene (57a, 14%), cis-2-benzoyl-1-cyclohexyl-3-phenylaziridine (46b, 35%) and benzoic acid (12a, 11%), along with a 40% recovery of the unchanged starting material (46a). Similarly, the reaction of 46b, under analogous conditions, gave a mixture of 57a (12%), the trans-aziridine 46a (40%) and 12a (10%), along with a 36% recovery of the unchanged starting material (46b). The isomerization of the starting aziridines 46a and 46b, on treatment with potassium in THF, saturated with oxygen may be understood in terms of the radical anion intermediates 50 and 58, as shown in Scheme III.6, which could get reconverted to the starting aziridines through back electron transfer to oxygen and thereby generating the superoxide anion, under these conditions. Yet another possible mode of transformation of the starting aziridines 46a,b is through a C-N bond cleavage, on treatment with potassium, to



Scheme III.6

give the radical anion intermediates 59(a,b), which can subsequently react with oxygen to give ultimately benzoic acid (12a), as shown in Scheme III.6.

It is pertinent to note that the isomerization of the aziridines 46a and 46b can also be brought about, by treatment with superoxide. Thus, the treatment of 46a with potassium superoxide in benzene in the presence of 18-crown-6 gave a mixture of 46b (36%), 12a (13%) and unchanged starting material (46a, 40%), whereas 46b, under analogous conditions gave a mixture of 46a (42%), 12a (10%) and unchanged starting material (46b, 38%).

The formation of both 64 and 68 in the reaction of 61 with potassium can be understood in terms of the pathways shown in Scheme III.6. The radical anion intermediate 62 can lead to 63 through the loss of a cyclohexyl fragment, which can then give rise to the isoquinoline derivative 64, through protonation, under the conditions of workup. The formation of 68, on the other hand, can be rationalized in terms of the reaction of 62 with oxygen, followed by further transformations, as shown in Scheme III.6.

To examine the involvement of oxygen in the reaction of 61, we have, in a separate experiment, carried out the reaction of 61 with potassium in THF, saturated with oxygen. Under these conditions, 61 gave a 8% yield of 68, besides a 70% recovery of the unchanged starting material (61). The relatively poor yield

of 68 and the recovery of most of the starting material (61), under these conditions would imply that most of the radical anion 62, formed from 61, is getting reconverted to the starting material by back electron transfer to oxygen and thereby generating superoxide anion. The starting aziridine 61 appears to be unreactive towards superoxide and in support of this view, it has been observed that treatment of 61 with potassium superoxide in benzene in the presence of 18-crown-6 did not give any isolable product; most of the starting material (61, 90%) was recovered unchanged.

III.4 CYCLIC VOLTAMMETRIC STUDIES¹²

As highlighted in earlier studies from this laboratory¹³⁻¹⁵ electrochemical investigations would prove valuable in the characterization of radical anions, the primary intermediates involved in the reaction of different unsaturated organic substrates with potassium in THF. In the present study, we have generated electrochemically the radical anions of the epoxyketones 1a,b, 34a,b and the aziridines 46a-d and 61. The cyclic voltammograms of 1a,b and 34a,b are shown in Figure III.2 and those of the aziridines 46a-d and 61 are shown in Figure III.3. The reduction peak potentials are summarized in Table III.1. All the epoxyketones 1a,b and 34a,b exhibited irreversible reduction peaks with the reduction potentials in the range of -1.32 to -2.90 V versus SSCE reference, whereas the aziridines 46a-d and 61

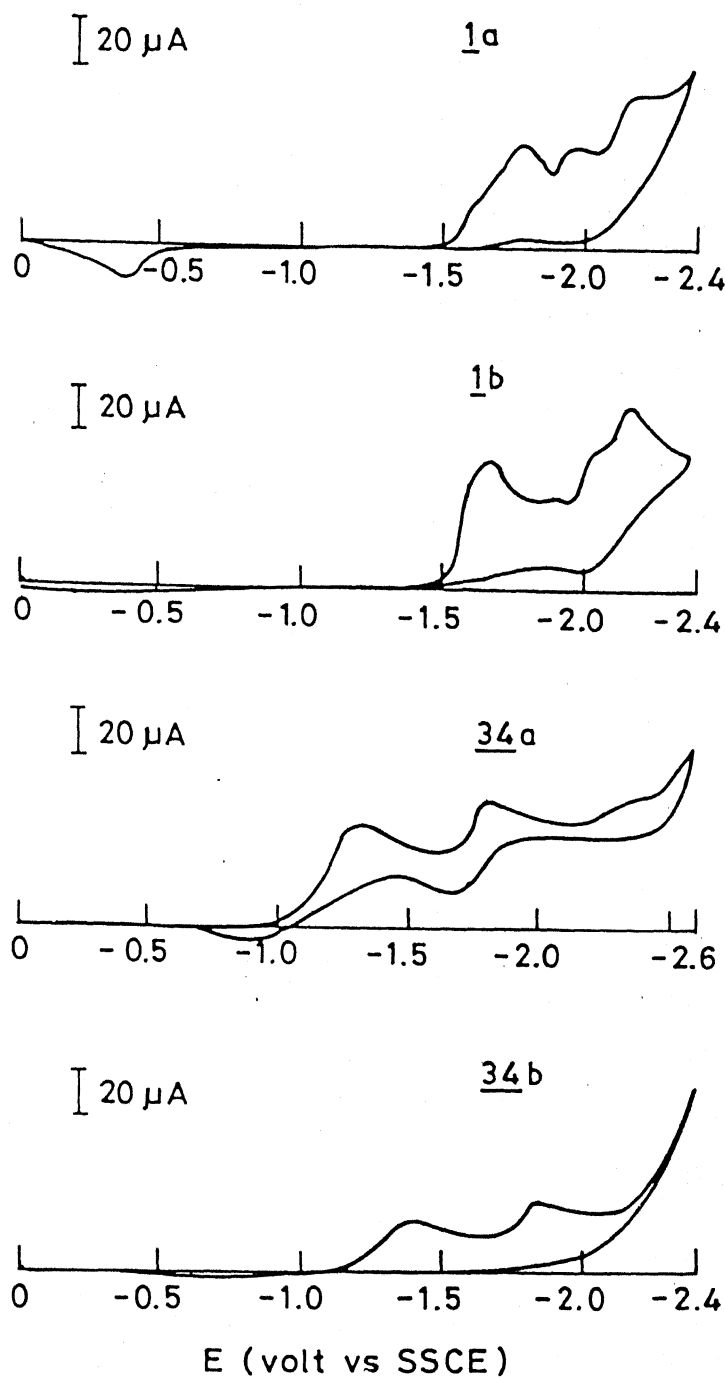


Figure III.2 Cyclic voltammograms of 1a,b and 34a,b

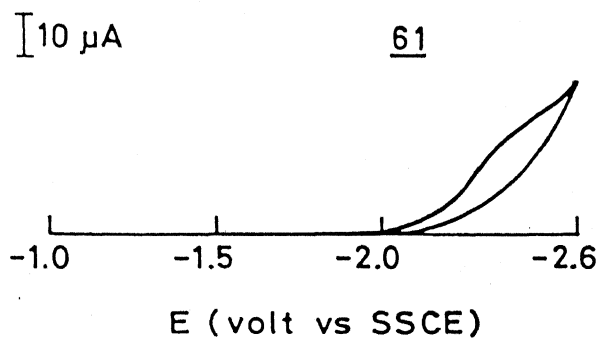
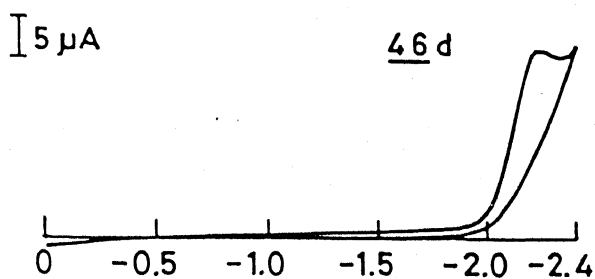
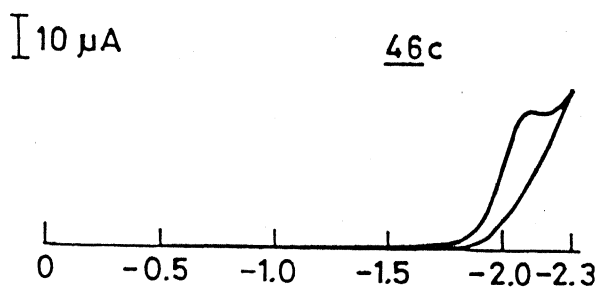
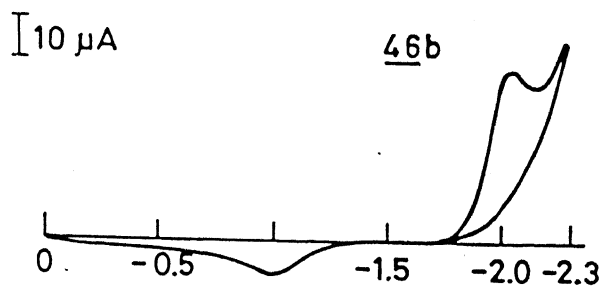
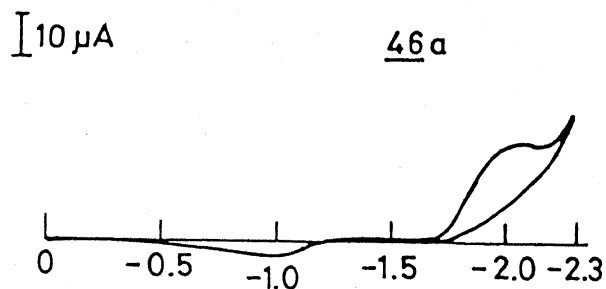


Figure III.3 Cyclic voltammograms of 46a-d and 61

Table III.1 Electrochemical, spectral and kinetic data of 1a,b, 34a,b, 46a-d and 61

Comp- ound	Reduction peak potential ^a E_p (V vs. Ag/Ag ⁺)	Absorption maxima ^b		$k^{b,c}$ ($10^{10} \text{ M}^{-1} \text{ s}^{-1}$) ± 0.2	$\tau_{1/2}^{b,d}$ (μs)
		Starting material	Radical anion		
<u>1a</u>	-1.79, -2.00, -2.19	246, 290(sh)	280, 310(sh), ~ 420	1.3	9
<u>1b</u>	-1.67, -2.06, -2.18	248, 278(sh)	330, ~ 460	1.2	119
<u>34a</u>	-1.32, -1.80, -2.30	248, 298(sh)	340, 460, 500	1.5	240
<u>34b</u>	-1.40, -1.84	256, 300(sh)	360, 500	1.2	1500
<u>46a</u>	-1.95	250, 278(sh)	340, ~ 450(sh)	1.4	143
<u>46b</u>	-1.94	246, 280(sh)	360, 440	1.2	575
<u>46c</u>	-1.98	246, 280(sh)	315, ~ 460(sh)	1.4	260
<u>46d</u>	-2.12	256, 290(sh)	325, 360(sh), 450	1.1	1400
<u>61</u>	-2.28	252, 292(sh)	285	1.3	3

a, In acetonitrile containing 0.1 M TBAP.

b, In methanol.

c, Rate constant for the reaction between the solvated electron and the substrate.

d, Half-life of the radical anion.

exhibited irreversible reduction peaks with the reduction potentials in the range of -1.94 to -2.28 V versus SSCE reference.

III.5 PULSE RADIOLYSIS STUDIES¹⁶

Earlier reports have shown that radical anions of unsaturated organic compounds can be generated through their reaction with solvated electrons (e^-_{sol}) under pulse radiolytic conditions.^{13-15,17-19} In the present study, the radical anions of epoxyketones 1a,b, 34a,b and the aziridines 46a-d and 61 were generated in methanol pulse radiolytically and their absorption spectra are presented in Figures III.4 and III.5. These radical anions exhibited strong absorption maxima in the region 280-500 nm. As is evident from Table III.1, these radical anions are formed from their appropriate precursors through the reaction with e^-_{sol} under diffusion controlled rates.

III.6 EXPERIMENTAL

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophotometers. The electronic spectra were recorded on Cary 17D or Cary 219 or Beckman DB spectrophotometers. NMR traces were recorded on Varian EM-390, CFT-80 or Bruker-400 MHz NMR spectrometers using tetramethylsilane as the internal standard. The mass spectra were recorded on a Hitachi RMU-6E single focussing mass spectro-

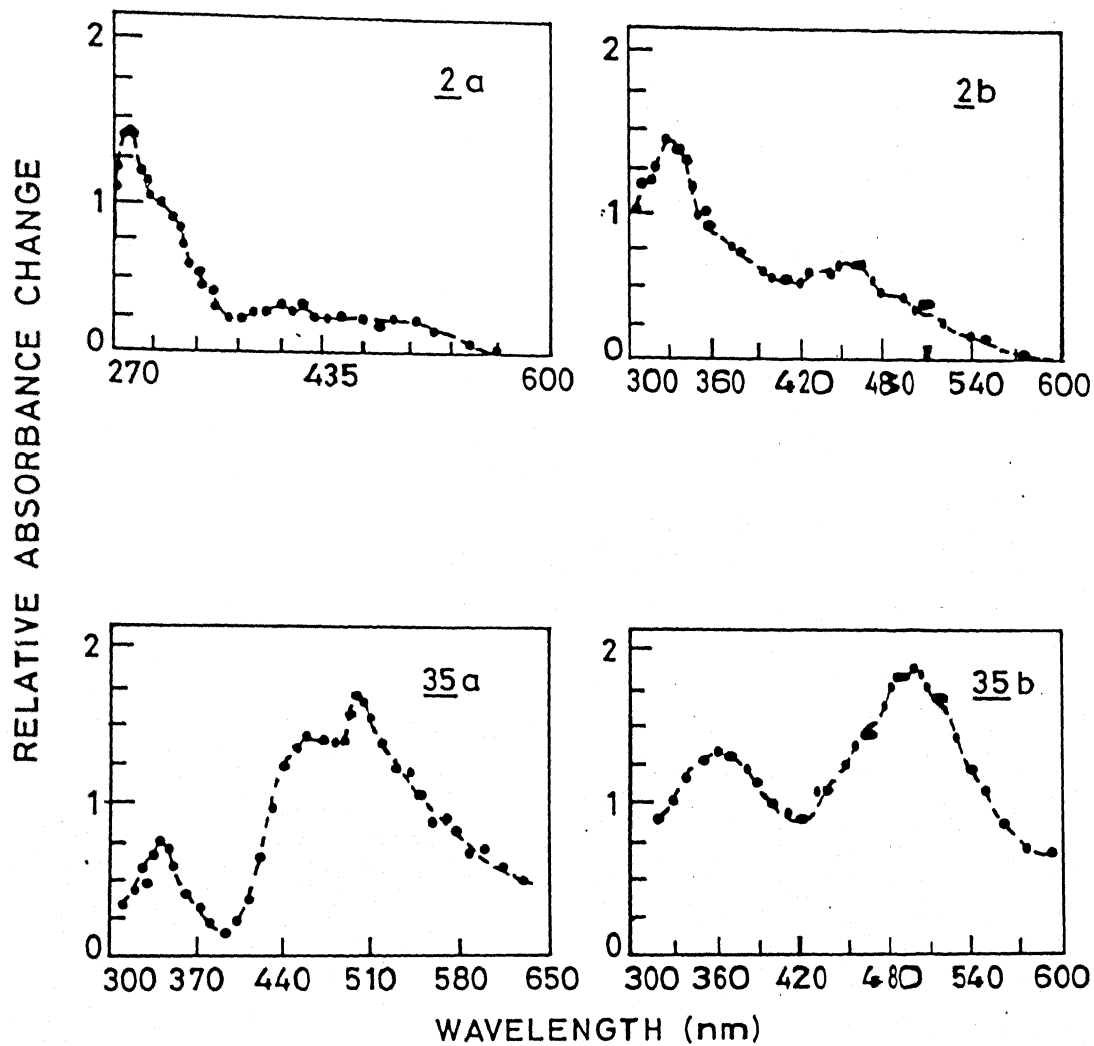


Figure III.4 Absorption spectra of the radical anions 2a,b and 35a,b

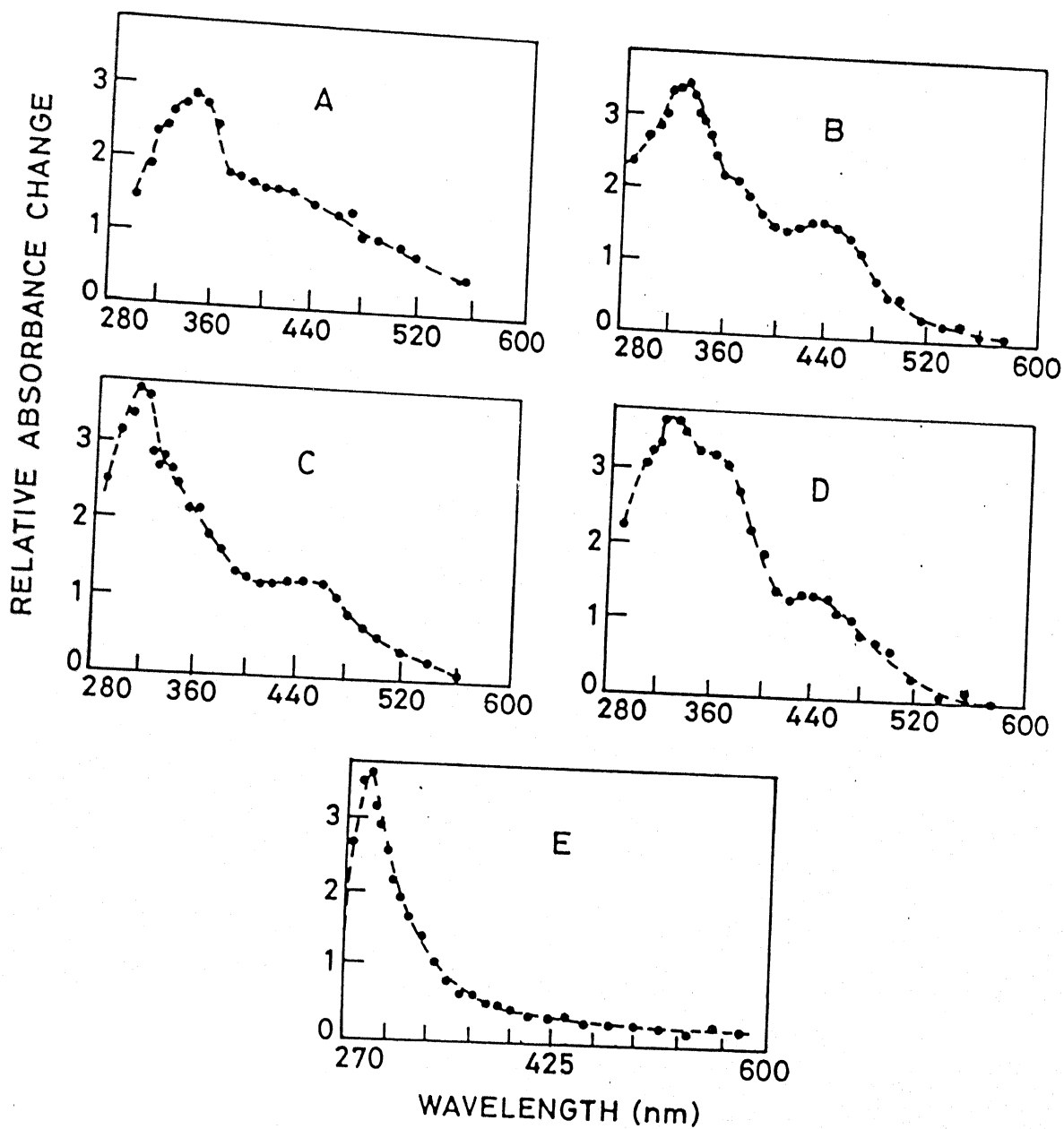


Figure III.5 Absorption spectra of the radical anions of 46a (A), 46b (B), 46c (C), 46d (D) and 61 (E)

meter or a Varian Mat CH7 mass spectrometer at 70 eV.

III.6.1 Starting Materials. trans-1,3-Diphenyl-2,3-epoxypropan-1-one (1a),²⁰ mp 90 °C, trans-2,3-epoxy-1-phenyl-3-p-tolylpropan-1-one (1b),²⁰ mp 96-97 °C, 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (34a),²¹ mp 122-123 °C, 2,3-dibenzoyl-1,4-dihydro-1,4-diphenyl-1,4-epoxynaphthalene (34b),²¹ mp 156-157 °C, trans-2-benzoyl-1-cyclohexyl-3-phenylaziridine (46a),²² mp 100-101 °C, cis-2-benzoyl-1-cyclohexyl-3-phenylaziridine (46b),²² mp 108-109 °C, cis-2-benzoyl-1-cyclohexyl-3-p-tolylaziridine (46c),²³ mp 118-119 °C, cis-1-cyclohexyl-2-phenyl-3-p-tolylaziridine (46d),²² mp 111-112 °C and 1-cyclohexyl-6-(cyclohexylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno-[1,2-b]arizine (61),²⁴ mp 159-160 °C were prepared by reported procedures. Petroleum ether used was the fraction with bp 60-80 °C. THF used was dried over sodium and was distilled immediately before use. Gold Label acetonitrile was used for cyclic voltammetric studies and spectral grade methanol (Fischer Scientific) was used for pulse radiolysis.

III.6.2 Reaction of Epoxyketones (1a,b, 34a,b), Benzoylaziridines (46a-d) and the Aziridine 61 with Potassium in THF.

A general procedure was to shake a mixture of the appropriate substrate (1a,b, 34a,b, 46a-d, 61) and excess of finely cut potassium (required equivalents) in THF (125 mL) in a stoppered round bottomed flask for several hours. A few clean, broken

glass pieces were added to the reaction mixture to ensure a fresh surface of the metal throughout the reaction. Pronounced colour changes were observed during the reaction due to the formation of radical anion and dianion intermediates. The mixture was poured into moist THF (100 mL), on completion, to destroy any unreacted potassium and the solvent was removed under reduced pressure to give a residual solid. This material was treated with water (10 mL) and extracted with methylene chloride (100 mL). Acidification of the aqueous layer with dilute hydrochloric acid and then extraction with methylene chloride or ethyl acetate gave the carboxylic acid fractions, which were recrystallized from suitable solvents. Workup of the non-aqueous fraction (methylene chloride extract) by removal of the solvent under reduced pressure and chromatographing the residual solid over silica gel, followed by recrystallization from suitable solvents gave the non-acidic products.

III.6.3 Reaction of *trans*-1,3-Diphenyl-2,3-epoxypropan-1-one (1a) with Potassium in THF. Treatment of 1a (1.12 g, 5 mmol) with potassium (195 mg, 5 mg-atom) in THF (125 mL) for 8 h and workup in the usual manner gave 400 mg (33%) of benzoic acid (12a), mp 121 °C, from the aqueous fraction, after recrystallization from petroleum ether and 310 mg (26%) of 2,3-diphenyl-2-hydroxypropanoic acid (15a), mp 163-164 °C (mixture mp),²⁵ after recrystallization from benzene. Removal of the solvent

from the non-aqueous fraction (methylene chloride extract) gave a product mixture, which was chromatographed over silica gel. Elution with petroleum ether gave 30 mg (5%) of acetophenone (13) (superimposable ir spectrum with that of an authentic sample). Further elution with a mixture (3:7) of benzene and petroleum ether gave 50 mg (5%) of 1,3-diphenylpropan-1-one (20a), mp 72-73 °C (mixture mp).²⁶ Continued elution with a mixture (2:3) of benzene and petroleum ether gave 35 mg (4%) of benzalacetophenone (4a), mp 56-57 °C (mixture mp). Subsequent elution with a mixture (3:2) of benzene and petroleum ether gave 100 mg (11%) of 5-benzoyl-1,3,4-triphenylcyclopent-1-ene (21a), mp 181-182 °C (mixture mp).²⁷ Further elution of the column with benzene gave 30 mg (3%) of 1-benzoyl-2,4,5-triphenylcyclopent-1-ene (22a), mp 122-123 °C (mixture mp).²⁷

In a repeat run, 1a (1.12 g, 5 mmol) was treated with potassium (195 mg, 5 mg-atom) in THF (125 mL), saturated with oxygen, for 8 h. Workup of the aqueous fraction as in the earlier case gave 300 mg (25%) of 12a, mp 121 °C (mixture mp) and 50 mg (4%) of 2,3-dihydroxy-2,3-diphenylpropanoic acid (33), mp 208-209 °C (mixture mp).²⁸ The non-aqueous fraction was worked up by removal of the solvent under vacuum and chromatographing the residue over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 100 mg (10%) of 20a, mp 72-73 °C (mixture mp). Further elution with a mixture (2:3) of benzene and petroleum ether gave 30 mg (3%) of benzalaceto-

phenone (4a), mp 56-57 °C (mixture mp). Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 150 mg (19%) of 1,2,4-triphenylbutan-1,4-dione (32), mp 125-126 °C (mixture mp).²⁹ Continued elution with a mixture (7:3) of benzene and petroleum ether gave 200 mg (18%) of the unchanged starting material (1a), mp 90 °C (mixture mp). Further elution of the column with benzene gave 75 mg (8%) of 2-hydroxy-2,4,5-triphenyl-3(2H)-furanone (31), mp 198-199 °C (mixture mp).³⁰

III.6.4 Reaction of Benzalacetophenone (4a) with Potassium in THF. A mixture of benzalacetophenone (4a) (1.04 g, 5 mmol) and potassium (195 mg, 5 mg-atom) in THF (125 mL) was shaken for 15 h. Workup of the reaction mixture as in the earlier cases gave 120 mg (20%) of benzoic acid (12a), mp 121 °C (mixture mp), from the aqueous fraction. The non-aqueous fraction was worked up by removal of the solvent under vacuum and chromatographing over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 270 mg (30%) of 1,3-diphenylpropan-1-one (20a), mp 72-73 °C (mixture mp). Subsequent elution with a mixture (4:1) of benzene and petroleum ether gave 40 mg (4%) of 1-benzoyl-2,4,5-triphenylcyclopent-1-ene (22a), mp 122-123 °C (mixture mp).

III.6.5 Reaction of trans-2,3-Epoxy-1-phenyl-3-p-tolylpropan-1-one (1b) with Potassium in THF. Treatment of 1b (1.9 g, 8 mmol) with potassium (310 mg, 8 mg-atom) in THF

(125 mL) for 15 h and workup in the usual manner gave a mixture of 310 mg (31%) of benzoic acid (12a), mp 121 °C (mixture mp) (recrystallization from petroleum ether), 75 mg (7%) of p-toluic acid (12b), mp 182 °C (mixture mp) (recrystallization from benzene) and 600 mg (29%) of 2-hydroxy-2-phenyl-3-p-tolylpropanoic acid (15b), mp 184-185 °C (mixture mp)³¹ (recrystallization from a mixture (4:1) of methylene chloride and petroleum ether), from the aqueous fraction. The non-aqueous fraction was worked up by removal of the solvent under vacuum and chromatographing the residual solid over silica gel. Elution with petroleum ether gave 50 mg (3%) of acetophenone (13) (superimposable ir spectrum with that of an authentic sample). Further elution with a mixture (1:9) of benzene and petroleum ether gave 70 mg (4%) of 1-phenyl-3-p-tolylpropan-1-one (20b), mp 36 °C (mixture mp).²⁶ Subsequent elution with a mixture (3:7) of benzene and petroleum ether gave 60 mg (3%) of 4-methylbenzalacetophenone (4b), mp 96-97 °C (mixture mp). Continued elution with a mixture (1:1) of benzene and petroleum ether gave 75 mg (4%) of 5-benzoyl-3,4-di-p-tolyl-1-phenylcyclopent-1-ene (21b), mp 152-153 °C (mixture mp).²⁷ Further elution with benzene gave 200 mg (11%) of 1-benzoyl-4,5-di-p-tolyl-2-phenylcyclopent-1-ene (22b), mp 171-172 °C (mixture mp),²⁷ after recrystallization from a mixture (4:1) of benzene and petroleum ether.

III.6.6 Reaction of 7-Oxa-2,3-dibenzoylbicyclo[2.2.1]-hepta-2,5-diene (34a) with Potassium in THF. Treatment of 34a

(600 mg, 2 mmol) with potassium (78 mg, 2 mg-atom) in THF (125 mL) for 7 h and workup as in the earlier cases gave 75 mg (15%) of benzoic acid (12a), mp 121 °C (mixture mp), from the aqueous fraction. Removal of the solvent from the non-aqueous fraction (methylene chloride extract) gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 30 mg (5%) of the unchanged starting material (34a), mp 122-123 °C (mixture mp). Subsequent elution with benzene gave 400 mg (70%) of o-dibenzoylbenzene (38a), mp 148-149 °C (mixture mp).³²

In a repeat run, 34a (600 mg, 2 mmol) was treated with potassium (78 mg, 2 mg-atom) in THF (125 mL), which was previously saturated with oxygen. Workup of the reaction mixture as in the earlier cases gave 125 mg (26%) of 12a, mp 121 °C (mixture mp) and 270 mg (45%) of the unchanged starting material (34a), mp 122-123 °C (mixture mp).

III.6.7 Reaction of 2,3-Dibenzoyl-1,4-dihydro-1,4-diphenyl-1,4-epoxynaphthalene (34b) with Potassium in THF. A solution of 34b (2.0 g, 4 mmol) in THF (125 mL) was shaken with potassium (156 mg, 4 mg-atom) for 15 h. Workup of the reaction mixture as in the earlier cases gave 400 mg (41%) of benzoic acid (12a), mp 121 °C (mixture mp), from the aqueous fraction. The non-aqueous fraction, on workup by removal of the solvent under vacuum, gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:9) of benzene and

petroleum ether gave 440 mg (41%) of 1,3-diphenylisobenzofuran (40b), mp 129-130 °C (mixture mp). Further elution of the column with a mixture (2:3) of benzene and petroleum ether gave 200 mg (13%) of 2-benzoyl-1,4-diphenylnaphthalene (45b), mp 126-127 °C (mixture mp) (lit. mp 124-127 °C).³³ Continued elution with a mixture (3:1) of benzene and petroleum ether gave 400 mg (21%) of 2,3-dibenzoyl-1,4-diphenylnaphthalene (38b), mp 185-186 °C (mixture mp).³⁴ Subsequent elution with benzene gave 150 mg (13%) of *o*-dibenzoylbenzene (38a), mp 148-149 °C (mixture mp).

In a repeat run, 1.0 g (2 mmol) of 34b was treated with 78 mg (2 mg-atom) of potassium in THF (125 mL), saturated with oxygen for 15 h. Workup as in the earlier cases gave 120 mg (25%) of 12a, mp 121 °C (mixture mp), 100 mg (19%) of 1,3-diphenylisobenzofuran (40b), mp 129-130 °C (mixture mp), 450 mg (45%) of the unchanged starting material (34b), mp 156-157 °C (mixture mp) and 100 mg (17%) of 38a, mp 148-149 °C (mixture mp).

III.6.8 Reaction of trans-1,3-Diphenyl-2,3-epoxypropan-1-one (1a) with Potassium Superoxide. A mixture of 1a (1.12 g, 5 mmol), potassium superoxide (710 mg, 10 mmol) and 18-crown-6 (660 mg, 2.5 mmol) in benzene (100 mL) was stirred at room temperature for 18 h, protected from sunlight. The reaction mixture became red initially and later turned to dark brown. On completion of the reaction, the mixture was washed several times with aqueous sodium chloride solution. Removal of the solvent from

the organic layer under vacuum gave a residual solid, which on fractional crystallization from a mixture (2:3) of benzene and petroleum ether gave 200 mg (18%) of the unchanged starting material (1a), mp 90 °C (mixture mp) and 150 mg (16%) of 2-hydroxy-2,4,5-triphenyl-3(2H)-furanone (31), mp 198-199 °C (mixture mp). The combined aqueous washings was acidified with dilute hydrochloric acid and extracted with ethyl acetate. Removal of the solvent gave a residue, which on fractional crystallization from a mixture (3:1) of methylene chloride and petroleum ether gave 450 mg (37%) of benzoic acid (12a), mp 121 °C (mixture mp) and 150 mg (12%) of 2,3-dihydroxy-2,3-diphenylpropanoic acid (33), mp 208-209 °C (mixture mp).

III.6.9 Reaction of 7-Oxa-2,3-dibenzoylbicyclo[2.2.1]-hepta-2,5-diene (34a) with Potassium Superoxide. A mixture of 34a (600 mg, 2 mmol), potassium superoxide (140 mg, 2 mmol) and 18-crown-6 (530 mg, 2 mmol) was stirred in benzene (100 mL) at room temperature for 30 h, protected from sunlight. Workup of the reaction mixture as in the earlier case gave 300 mg (50%) of the unchanged starting material (34a), mp 122-123 °C (mixture mp), from the non-aqueous fraction and 100 mg (20%) of benzoic acid (12a), mp 121 °C (mixture mp), from the aqueous washings.

III.6.10 Reaction of 2,3-Dibenzoyl-1,4-dihydro-1,4-diphenyl-1,4-epoxynaphthalene (34b) with Potassium Superoxide.

A mixture of 34b (1.0 g, 2 mmol), potassium superoxide (140 mg, 2 mmol) and 18-crown-6 (265 mg, 1 mmol) in benzene (100 mL) was stirred at room temperature for 20 h, protected from sunlight and worked up as in the earlier cases. Removal of the solvent under vacuum from the non-aqueous fraction gave a mixture of products, which was chromatographed over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 120 mg (22%) of 1,3-diphenylisobenzofuran (40b), mp 129-130 °C (mixture mp). Further elution with a mixture (7:3) of benzene and petroleum ether gave 500 mg (50%) of the unchanged starting material (34b), mp 156-157 °C (mixture mp). Subsequent elution of the column with benzene gave 120 mg (21%) of o-dibenzoylbenzene (38a) mp 148-149 °C (mixture mp). Workup of the aqueous fraction gave 125 mg (26%) of benzoic acid (12a), mp 121 °C (mixture mp).

III.6.11 Reaction of trans-2-Benzoyl-1-cyclohexyl-3-phenylaziridine (46a) with Potassium in THF. Treatment of 46a (610 mg, 2 mmol) with potassium (78 mg, 2 mg-atom) in THF (125 mL) for 10 h and workup in the usual manner gave 90 mg (37%) of benzoic acid (12a), mp 121 °C (mixture mp), from the aqueous fraction. Removal of the solvent from the non-aqueous fraction (methylene chloride extract) under reduced pressure gave a product mixture, which was chromatographed over silica gel. Elution with petroleum ether gave 55 mg (31%) of trans-stilbene (57a), mp 124 °C (mixture mp). Further elution with benzene gave 240 mg (37%) of N-cyclohexyl-2,3-diphenyl-

2-hydroxypropanamide (51a), mp 172-173 °C.

IR spectrum ν_{\max} (KBr): 3380 (OH), 3220 (NH), 3060, 3030, 2920 and 2840 (CH) and 1640 (C=O) cm^{-1} .

UV spectrum λ_{\max} (methanol): 216 nm (ϵ , 11,800) and 260 (500).

^1H NMR spectrum (CDCl_3): δ 0.8-1.9 (m, 10 H, cyclohexyl), 2.9 (s, 1 H, OH, D_2O exchangeable), 3.45 (q, 2 H, $J = 14$ Hz, methylene), 3.6 (m, 1 H, methine), 6.45 (broad, 1 H, NH) and 7.1-7.9 (m, 10 H, aromatic).

^{13}C NMR spectrum (CDCl_3): δ 21.04, 24.68, 25.51, 32.61, 32.76, 45.20, 47.98, 78.76 (C-OH), 125.54, 127.43, 128.07, 129.08, 130.50, 132.44, 136.54, 143.01 and 172.32 (C=O).

Mass spectrum, m/e (relative intensity): 323 (M^+ , 1), 232 ($\text{M}^+ - \text{C}_6\text{H}_5\text{CH}_2$, 10), 198 (23), 197 ($\text{M}^+ - \text{CONHC}_6\text{H}_{11}$, 100), 179 ($\text{M}^+ - \text{CONHC}_6\text{H}_{11}$, H_2O , 3), 165 (2), 150 (2), 122 (3), 120 (6), 105 (76) and other peaks.

Anal. Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_2$: C, 78.01; H, 7.74; N, 4.33.
Found: C, 78.42; H, 8.07; N, 4.07.

In yet another run, 46a (1.0 g, 3.27 mmol) was treated with potassium (128 mg, 3.27 mg-atom) in THF (125 mL), saturated with oxygen, for 15 h and worked up in the usual manner to give 40 mg (11%) of 12a, mp 121 °C (mixture mp), from the aqueous fraction. Removal of the solvent under vacuum from the non-aqueous fraction (methylene chloride extract) gave a residual

solid, which was chromatographed over silica gel. Elution with petroleum ether gave 40 mg (14%) of trans-stilbene (57a), mp 124 °C (mixture mp). Further elution with a mixture (2:3) of benzene and petroleum ether gave 400 mg (40%) of the unchanged starting material (46a), mp 100-101 °C (mixture mp). Subsequent elution with a mixture (3:2) of benzene and petroleum ether gave 350 mg (35%) of cis-2-benzoyl-1-cyclohexyl-3-phenylaziridine (46b), mp 108-109 °C (mixture mp).

III.6.12 Preparation of N-Cyclohexyl-2,3-diphenyl-2-hydroxypropanamide (51a). A mixture of 2,3-diphenyl-2-hydroxypropanoic acid (15a) (1.0 g, 4.1 mmol) and N,N-dimethylaniline (600 mg, 5 mmol) in dry ether (50 mL) was refluxed for 0.5 h. Freshly distilled acetyl chloride (390 mg, 5 mmol) was added to it, at such a rate that moderate refluxing was maintained even after the source of heat was removed. The reaction mixture was further refluxed for 0.5 h, cooled and was treated with water (50 mL). The ether layer was washed with 25 mL portions of cold dilute sulphuric acid several times and then with saturated sodium bicarbonate solution (20 mL). Afterwards, it was dried over magnesium sulphate and the solvent was removed under vacuum to give 850 mg (81%) of 2-acetoxy-2,3-diphenylpropanoic acid.

IR spectrum ν_{max} (KBr): 3500-2500 (OH) and 1730 (C=O) cm^{-1} .

Thionyl chloride (600 mg, 5 mmol) was added to this acid (850 mg, 3.3 mmol) and the mixture was refluxed for 1 h, followed by removal of the unchanged thionyl chloride by distillation. The acid chloride, thus obtained, was added drop-wise to a mixture of cyclohexylamine (485 mg, 5 mmol) and 2 N sodium hydroxide solution (50 mL). Extraction with methylene chloride and removal of the solvent under reduced pressure gave 550 mg (50%) of 2-acetoxy-N-cyclohexyl-2,3-diphenylpropanamide, mp 166-167 °C, after recrystallization from benzene.

IR spectrum ν_{max} (KBr): 3350 (NH), 3060, 3020, 2920 and 2840 (CH), 1730 and 1650 (C=O) cm^{-1} .

This ester (550 mg, 1.6 mmol) was hydrolysed by refluxing with 10% sodium hydroxide solution (50 mL) for 1 h. Extraction with methylene chloride and removal of the solvent under vacuum gave 325 mg (63%) of N-cyclohexyl-2,3-diphenyl-2-hydroxypropanamide (51a), mp 172-173 °C, after recrystallization from a mixture (2:3) of methylene chloride and petroleum ether.

III.6.13 Reaction of *cis*-2-Benzoyl-1-cyclohexyl-3-phenylaziridine (46b) with Potassium in THF. Treatment of 46b (610 mg, 2 mmol) with potassium (78 mg, 2 mg-atom) in THF (125 mL) for 10 h and workup in the usual manner gave 95 mg (39%) of benzoic acid (12a), mp 121 °C (mixture mp), from the aqueous fraction. Removal of the solvent from the non-aqueous fraction (methylene chloride extract) gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 60 mg

(33%) of trans-stilbene (57a), mp 124 °C (mixture mp). Further elution with benzene gave 220 mg (34%) of N-cyclohexyl-2,3-diphenyl-2-hydroxypropanamide (51a), mp 172-173 °C.

In a repeat run, 46b (1.0 g, 3.27 mmol) was treated with potassium (128 mg, 3.27 mg-atom) for 10 h in THF (125 mL), saturated with oxygen. Workup of the reaction mixture in the usual manner gave 40 mg (10%) of 12a, mp 121 °C (mixture mp), from the aqueous fraction. The non-aqueous fraction was worked up by removal of the solvent under vacuum and chromatographing the residual solid over silica gel. Elution with petroleum ether gave 35 mg (12%) of trans-stilbene (57a), mp 124 °C (mixture mp). Further elution with a mixture (2:3) of benzene and petroleum ether gave 400 mg (40%) of trans-2-benzoyl-1-cyclohexyl-3-phenylaziridine (46a), mp 100-101 °C (mixture mp). Subsequent elution with a mixture (3:2) of benzene and petroleum ether gave 360 mg (36%) of the unchanged starting material (46b), mp 108-109 °C (mixture mp).

III.6.14 Reaction of cis-2-Benzoyl-1-cyclohexyl-3-p-tolylaziridine (46c) with Potassium in THF. A mixture of 46c (640 mg, 2 mmol) and potassium (78 mg, 2 mg-atom) in THF (125 mL) was shaken for 24 h. Workup as in the earlier cases gave 95 mg (39%) of benzoic acid (12a), mp 121 °C (mixture up), from the aqueous fraction. The non-aqueous fraction was worked up by removal of the solvent under vacuum and chromatographing over silica gel. Elution with petroleum ether gave 60 mg (29%) of

trans-1,2-di-*p*-tolylethylene (57c), mp 179 °C (mixture mp).³⁵ Further elution with benzene gave 220 mg (33%) of N-cyclohexyl-2-hydroxy-2-phenyl-3-*p*-tolylpropanamide (51c), mp 152-153 °C.

IR spectrum ν_{\max} (KBr): 3380 (OH), 3210 (NH), 3060, 3020, 2930 and 2840 (CH) and 1640 (C=O) cm^{-1} .

UV spectrum λ_{\max} (methanol): 218 nm (ϵ , 15,000) and 260 (600).

¹H NMR spectrum (CDCl₃): δ 0.7-1.95 (m, 10 H, cyclohexyl), 2.25 (s, 3 H, methyl), 2.75 (s, 1 H, OH, D₂O exchangeable), 3.5 (q, 2 H, J = 14 Hz, methylene), 3.65 (m, 1 H, methine), 6.6 (broad, 1 H, NH) and 7.05-7.9 (m, 9 H, aromatic).

Anal. Calcd for C₂₂H₂₇NO₂: C, 78.33; H, 8.01; N, 4.15. Found: C, 78.68; H, 8.26; N, 4.27.

III.6.15 Reaction of *cis*-1-Cyclohexyl-2-phenyl-3-*p*-toluyl-aziridine (46d) with Potassium in THF. Treatment of 46d (500 mg, 1.56 mmol) with potassium (60 mg, 1.56 mg-atom) in THF (125 mL) for 24 h and workup in the usual manner gave 80 mg (38%) of *p*-toluic acid (12b), mp 182 °C (mixture mp), from the aqueous fraction. The non-aqueous fraction was worked up by removal of the solvent under reduced pressure and chromatographing the residue over silica gel. Elution with petroleum ether gave 50 mg (36%) of trans-stilbene (57a), mp 124 °C (mixture mp). Subsequent elution with benzene gave 220 mg (42%) of N-cyclohexyl-2-hydroxy-3-phenyl-2-*p*-tolylpropanamide (51d),

mp 185-186 °C.

IR spectrum ν_{max} (KBr): 3380 (OH), 3210 (NH), 3080, 3060, 3030, 2920 and 2840 (CH) and 1640 (C=O) cm^{-1} .

UV spectrum λ_{max} (methanol): 218 nm (ϵ , 17,000) and 260 (600).

^1H NMR spectrum (CDCl_3): δ 0.8-2.0 (m, 10 H, cyclohexyl), 2.38 (s, 3 H, methyl), 2.8 (s, 1 H, OH, D_2O exchangeable), 3.5 (q, 2 H, $J = 14$ Hz, methylene), 3.75 (m, 1H, methine), 6.65 (broad, 1 H, NH) and 7.1-8.0 (m, 9 H, aromatic).

Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_2$: C, 78.33; H, 8.01; N, 4.15.
Found: C, 78.13; H, 8.32; N, 4.63.

III.6.16 Reaction of 1-Cyclohexyl-6-(cyclohexylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-b]azirine (61) with Potassium. A solution of 61 (1.0 g, 2.6 mmol) in THF (125 mL) was shaken with potassium (100 mg, 2.6 mg-atom) for 12 h. The reaction mixture was worked up in the usual manner. The aqueous fraction, on acidification and extraction with methylene chloride, did not give any isolable product. Removal of the solvent from the non-aqueous fraction gave a product mixture, which was chromatographed over silica gel. Elution with a mixture (4:1) of benzene and petroleum ether gave 500 mg (64%) of 1-phenyl-4-cyclohexylaminoisoquinoline (64), mp 123-124 °C (mixture mp).³⁶ Further elution of the column with benzene gave 100 mg (13%) of 2-cyclohexyl-3-hydroxy-3-phenylphthalimidine (68),

mp 225-226 °C (mixture mp),³⁷ after recrystallization from a mixture (2:3) of methylene chloride and ethanol.

In a repeat run, 61 (500 mg, 1.3 mmol) was treated with potassium (50 mg, 1.3 mg-atom) in THF (125 mL), saturated with oxygen, for 12 h and worked up as in the earlier case to give 350 mg (70%) of the unchanged starting material (61), mp 159-160 °C (mixture mp) and 30 mg (8%) of 68, mp 225-226 °C (mixture mp).

III.6.17 Reaction of trans-2-Benzoyl-1-cyclohexyl-3-phenylaziridine (46a) with Potassium Superoxide. A mixture of 46a (500 mg, 1.63 mmol), potassium superoxide (115 mg, 1.63 mmol) and 18-crown-6 (264 mg, 1 mmol) in benzene (100 mL) was stirred at room temperature for 24 h, protected from sunlight. On completion of the reaction, the mixture was washed several times with aqueous sodium chloride solution. Removal of solvent from the organic fraction under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 200 mg (40%) of the unchanged starting material (46a), mp 100-101 °C (mixture mp). Further elution with a mixture (1:1) of benzene and petroleum ether gave 180 mg (36%) of cis-2-benzoyl-1-cyclohexyl-3-phenylaziridine (46b), mp 108-109 °C (mixture mp).

Workup of the combined aqueous fractions by acidification with dilute hydrochloric acid and extraction with methylene

chloride gave 25 mg (13%) of benzoic acid (12a), mp 121 °C (mixture mp).

III.6.18 Reaction of *cis*-2-Benzoyl-1-cyclohexyl-3-phenylaziridine (46b) with Potassium Superoxide. A mixture of 46b (500 mg, 1.63 mmol), potassium superoxide (115 mg, 1.63 mmol) and 18-crown-6 (264 mg, 1 mmol) in benzene (100 mL) was stirred at room temperature for 24 h, protected from sunlight and worked up as in the earlier case. Removal of the solvent from the organic fraction gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 210 mg (42%) of trans-2-benzoyl-1-cyclohexyl-3-phenylaziridine (46a), mp 100-101 °C (mixture mp). Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 190 mg (38%) of the unchanged starting material (46b), mp 108-109 °C (mixture mp). Workup of the aqueous fraction gave 20 mg (10%) of benzoic acid (12a), mp 121 °C (mixture mp).

III.6.19 Reaction of 1-Cyclohexyl-6-(cyclohexylimino)-1,1a,6,6a-tetrahydro-1a-phenylindeno[1,2-b]azirine (61) with Potassium Superoxide. A mixture of 61 (500 mg, 1.3 mmol), potassium superoxide (92 mg, 1.3 mmol) and 18-crown-6 (264 mg, 1 mmol) in benzene (100 mL) was stirred at room temperature for 36 h, protected from sunlight and worked up as in the earlier cases. Removal of the solvent from the non-aqueous fraction gave 450 mg (90%) of the unchanged starting material (61),

mp 159-160 °C (mixture mp). Workup of the aqueous fraction in the usual manner did not give rise to any isolable product.

III.6.20 Cyclic Voltammetry. Measurements were made with a Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat, PAR Model 175 Universal Programmer and Kipp and Zonen X-Y recorder. Experiments were performed in a standard three compartment cell equipped with a Pt-disc working electrode, a Pt-wire counter electrode and saturated sodium chloride-calomel electrode (SSCE) as reference. The cyclic voltammograms were recorded in deaerated acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP). The direction of the initial scan was cathodic and the scan rate was 200 mV/s.

III.6.21 Pulse Radiolysis. The description of the pulse radiolysis apparatus which allows the determination of the transient spectra at various time intervals after the pulse and kinetic measurements of the spectral changes has been reported earlier.³⁸ The irradiation was carried out with 5 ns pulses from the Notre Dame 8 MeV ARCO LP-7 linear accelerator, using dose rates of $\sim 2 \times 10^{16}$ eV/g per pulses. The solutions of the appropriate substrates in methanol were deaerated before pulse radiolysis by bubbling nitrogen for at least half an hour and the deaeration was continued in the reservoir from which the solution was allowed to flow slowly and continuously through

the cell. The rate constants for the reactions with solvated electrons (e^-_{sol}) were determined from the kinetic analysis of the enhanced rate of decay of e^-_{sol} in the presence of the appropriate substrate or from the growth rate of the radical anion.

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